On-demand electrostatic droplet charging and sorting

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This study reports a droplet-based microfluidic device for on-demand electrostatic droplet charging and sorting. This device combines two independent modules: one is a hydrodynamic flow focusing structure to generate water-in-oil droplets, and the other is the two paired-electrodes for charging and sorting of the droplets. Depending on the polarity on charging electrodes, water-in-oil droplets can be electrostatically charged positively or negatively, followed by automatic real-time electric sorting. This approach will be useful when preformed droplets, with a positive, a negative, or with no charge, need to be manipulated for further on-chip droplet manipulation. © 2011 American Institute of Physics. [doi:10.1063/1.3604393]

I. INTRODUCTION

Droplet-based microfluidics has emerged as one of the promising microfluidic platforms with significant advantages of high-throughput, continuous-flow, and ultralow-volume studies of biological and chemical experimentation.^{1,2} Another key advantage in droplet-based microfluidics lies in the ability to manipulate and analyze individual droplets.^{3,4} Recently, many research groups have approached droplet sorting with different kinds of sorting sources (e.g., passive or active). Passive sorting methods employ channel geometry^{5,6} or gravity⁷ to sort droplets in a microfluidic channel by its size. Active sorting methods typically use dielectrophoresis (DEP),^{8–10} surface acoustic wave (SAW),¹¹ laser,¹² or electric force.^{4,13} Most of the droplet sorting methods control droplets in a binary mode (keep or discard), and have limited functionality to manipulate the sorted droplets for further post-process. In our previous work, we have demonstrated concurrent droplet charging and sorting by electrostatic induction on droplet formation.¹³ However, the method is not compliant for manipulating preformed or reloaded uncharged/charged droplets. In this work, we have investigated an on-demand robust electrostatic droplet charging and sorting mechanism. This approach will be useful when preformed or reloaded droplets need to be manipulated for further on-chip operation.

II. METHODS AND MATERIALS

A. Working mechanism

Figure 1 shows the schematic illustration of the on-demand electrostatic droplet charging and sorting device. The device consists of two modules: a hydrodynamic flow focusing structure to generate water-in-oil droplets (which is not shown) and a two-paired-electrode system. A charging electrode (CE) and a ground electrode are placed perpendicular to the flow direction in a narrow channel for electrostatic droplet charging. A sorting electrode (SE) and a ground electrode are placed parallel to the flow direction across a sorting channel for electric droplet sorting. The spacing of the charging electrodes (s), the width of the charging channel (w_C) and the width of the sorting channel (w_S) are defined for future analysis as indicated in Fig. 1(a). When a preformed droplet is squeezed in the narrow channel, a positive or negative pulse will be applied to the charging electrode to induce an opposite charge on the water–oil interface. While the water-in-oil droplet leaves the charging electrode, the induced charge will be trapped and uniformly distributed

FIG. 1. Working principle of the proposed device. Once a preformed, uncharged, water-in-oil droplet is electrostatically charged, it is sorted by its polarity. The dotted lines show the border between laminar flow streams for each outlet. In our design, the height of the microfluidic channels is 50 μm , the width of the narrow channel is 40 μm , and the width of the sorting channel is 200 μm . (a) Top view and (b) cross-sectional view.

on the surface of the droplet. During this charging process, negative or positive charges are charged from the ground electrode, not simply induced. The charging electrode can be switched in real-time to induce different amount and polarity of charge on the droplets. Unlike the charging electrode, only positive potential is applied to the sorting electrode, causing attraction of the negatively charged droplets. This pulls the negatively charged droplets to flow to the upper channel of the outlet, while the positively charged droplets are pushed downwards, and the uncharged droplets move straight into the middle channel.

A charged droplet would experience an electric force, $F_E = qE_S$, in the sorting channel, where q is the surface charge on the droplet induced by the charging electrode and E_S is the electric field applied across the two sorting electrodes. However, we need to include a viscous drag force, F_D , to calculate the net force on the charged droplet in the oil carrier medium. Thus, the total force acting on the charged droplet is

$$m \frac{d^2 y}{dt^2} = F_E + F_D = qE_S - 6\pi r \eta \frac{dy}{dt}, \quad (1)$$

where y is the deflection of the droplet perpendicular to the flow direction in the sorting channel, m is the mass of the droplet, r is the radius of the droplet, η is the dynamic viscosity of the carrier medium, and t is the traveling time of the droplet along the sorting electrode. Solving (1) for y , we obtain

$$y = \frac{qE_S}{6\pi r \eta} t + \frac{qE_S m}{(6\pi r \eta)^2} (e^{-(6\pi r \eta/m)t} - 1). \quad (2)$$

In (2), the second term becomes negligible due to the small size of our droplet (e.g., $r = 35 \mu\text{m}$): $t/r \gg 2\rho r/9\eta$, where ρ is the density of the droplet. Thus, the deflection y of the charged droplet

in the sorting channel is proportional to its induced charge (q), sorting voltage (V_S), traveling time (t), and inversed droplet size (r^{-1}):

$$y \propto qV_S t r^{-1}. \quad (3)$$

The droplet size is controlled by the relative volumetric flow rates of the oil (Q_{oil}) and the water (Q_{water}) at the hydrodynamic flow focusing structure. The traveling time is determined by the net flow rate, which is the sum of Q_{oil} and Q_{water} . The amount and polarity of the induced charge is dependent on the charging voltage (V_C) applied to the preformed droplet. When such parameters are fixed, the key parameter to affect the deflection y is the sorting voltage (V_S): $y \propto V_S$. For example, to successfully sort out a negatively charged droplet, we need to deflect it at least $y > y_{min}$, where it can cross over the border of two streams ($y = y_{min}$) [see the dotted line in Fig. 1(a)]. When we apply the sorting voltage of $V_S > V_{S_min}$, the droplet lies within the laminar flow stream of the upper channel, causing the droplet to flow to the upper channel.

B. Device fabrication and materials

The device was fabricated using soft lithography to form microfluidic channels in polydimethylsiloxane (PDMS)¹⁴ and photolithography to define the electrodes on a glass substrate. To prepare the soft mold for the channels, negative photoresist (SU-8 2050) was spin-coated and patterned on a silicon wafer. From the mold, PDMS replica was formed, followed by punching for inlets and outlets. Indium tin oxide (ITO, 100 nm thick) electrodes were deposited by DC sputter on the patterned glass substrate, and a lift-off process was performed to finalize the conductive ITO electrodes.^{15,16} An oxide insulation layer (300 nm) was grown over the electrodes using PECVD. Then a square window ($40 \times 40 \mu\text{m}^2$) was etched over the ground electrode in the narrow channel to allow an electric contact to the droplets. Finally, the electrode-patterned glass substrate and the PDMS microfluidic channels molded from the soft mold were exposed to O_2 plasma and were bonded irreversibly. This was followed by baking them over a hot plate for 24 h at 70°C to improve the bonding strength between the oxide layer and the PDMS. De-ionized (DI) water and mineral oil were used as aqueous and oil phases, respectively, and nonionic surfactant (2% span-20) was added into the mineral oil to prevent droplet coalescence. The use of the nonionic surfactant minimizes the possible electrokinetic effects that can be expected during the electrostatic actuation. The voltage was supplied by a high-voltage source (HVS448-1500, Lab-Smith, Livermore, CA) connected to a computer controller, and all the experiments results were captured by a Nikon stereo-type microscope.

III. RESULTS AND DISCUSSION

First, we demonstrated that droplets could be electrostatically charged negatively or positively (depending on the polarity on the charging electrode), followed by an automatic real-time electric sorting. Water and oil flow rates were set at 15 and $75 \mu\text{l/h}$, respectively, and the corresponding droplet size was $67\text{--}71 \mu\text{m}$. In our device, the channel width was $200 \mu\text{m}$ and the minimum deflection value for successful sorting was $y_{min} \sim 33 \mu\text{m}$. Applying this to Eqs. (2) and (3), this value lead to a minimum sorting voltage of $V_{S_min} \sim 80 \text{ V}$. To ensure successful sorting, we increased the value of V_S up to 110 V, which corresponded to the deflection of $y = 45 \mu\text{m}$. In this calculation, the amount of charge on the droplet which is charged from the ground electrode would equal to $3.5 \times 10^{-14} \text{ C}$ when $y = 45 \mu\text{m}$, $r = 35 \mu\text{m}$, $m = 180 \times 10^{-12} \text{ kg}$, $E_S = 366 \text{ kV/m}$, $t = 65 \text{ ms}$, and $\eta = 28.1 \text{ mPa s}$. The values for y , r , m , and t were empirically obtained from experimental data shown in Fig. 2. E_S was determined by applied sorting voltage, and η was from the carrier oil property. The fringe effect due to the sorting electrodes was ignored during the calculation.

Figure 2 shows the time lapse trace lines for negatively and positively charged droplets. For a negatively charged droplet, we applied a positive charging voltage of $V_C = +80 \text{ V}$ and a positive sorting voltage of $V_S = +110 \text{ V}$ [Fig. 2(a)]. One can notice that the negatively charged droplet follows the center line (dotted line) until it reaches the sorting electrode area: $y = 0 \mu\text{m}$ when t

FIG. 2. Photographs of charged droplets with different polarity. (a) A negatively charged droplet flowing into the upper outlet ($V_C = +80$ V and $V_S = +110$ V). (b) A positively charged droplet flowing into the lower outlet ($V_C = -80$ V and $V_S = +110$ V).

~ 15 ms. Beyond that point the droplet moved upwards from the center line: $y = \sim 45$ μm when $t = \sim 80$ ms. For a positively charged droplet, we applied the same voltage for both the charging and sorting electrodes but with a different charging polarity: $V_C = -80$ V and $V_S = +110$ V [Fig. 2(b)]. With this change, the droplet was positively charged and sorted to the lower outlet channel.

Next, we performed continuous and selective droplet charging and sorting. When negatively charged droplets reached the sorting channel with no potential ($V_S = 0$ V), all charged droplets flowed into the middle channel due to the lack of the sorting force and the laminar nature of the stream [Fig. 3(a)]. On the other hand, when a sorting voltage of $V_S = +110$ V was applied at the sorting electrode, the negatively charged droplets were continuously sorted to the upper channel [Fig. 3(b)]. We also demonstrated selective charging and sorting by employing a pulsed charging voltage [Figs. 3(c) and 3(d)]. In this case, we applied the same magnitude with $V_C = +80$ V and $V_S = +110$ V, but applied a pulsed potential to the charging electrode to allow selective droplet charging. The pulse applied to the charging electrode was 60 and 90 ms and the corresponding number of uncharged droplets was 2 and 3 in Figs. 3(c) and 3(d), respectively. While the charged droplets were continuously sorted to the upper or the lower channel, the uncharged droplets flowed to the middle channel due to the lack of its surface charges. If coupled to a detection unit, the proposed droplet charging and sorting device can be applied for on-demand droplet manipulation by comparing the detected results to specific criteria in a fluorescence activated manner, as in a conventional fluorescence activated cell sorting system (FACS).

Finally, we studied the droplet charging and sorting mechanism as functions of the droplet size and sorting voltage. Figure 4 shows a summary of the working conditions of the droplet charging and sorting. The droplet size was controlled by the relative volumetric flow rates of the oil (Q_{oil}) and the water (Q_{water}) at the hydrodynamic flow focusing structure. The flow rate ratio, $Q_{\text{ratio}} = Q_{\text{oil}} / Q_{\text{water}}$, was varied from 2 to 7, while the sum of Q_{oil} and Q_{water} was fixed to 90 $\mu\text{l/h}$. In this experiment, we applied the charging voltage of $V_C = +80$ V [Fig. 4(c)], and $V_C = -80$ V [Fig. 4(d)], and varied the sorting voltage for each flow rate ratio. We categorized the working condition into three zones: zone (i) for stable charging and sorting, zone (ii) for stable charging but unstable sorting, and zone (iii) for no charging and no sorting.

FIG. 3. Photographs of the proposed device. (a) No sorting of the negatively charged droplets when $V_C=80$ V and $V_S=0$ V. (b) Continuous sorting of the negatively charged droplets when $V_C=80$ V and $V_S=110$ V. (c) and (d) Selective charging and sorting with different pulses for the charging electrode when $V_C=80$ V (pulsed) and $V_S=110$ V. The pulse applied to the charging electrode was 60 ms and 90 ms in (c) and (d), respectively.

As previously discussed, the sorting voltage must be larger than the minimum sorting voltage ($V_S > V_{S_min}$), in order for the droplets to deflect from the middle stream to the upper or lower stream: $V_S = V_{S_min}$ at $y = y_{min}$. Also, the center of the charged droplet should lie within the laminar flow stream of the upper or lower channels, to cause the droplet to flow to the corresponding channel. Thus, the maximum diameter of the droplet d_{max} has to satisfy the following condition:

$$d_{max} = w_S - 2y_{min}, \quad (4)$$

where w_S is the width of the sorting channel [Fig. 1(a)]. Furthermore, the squeezed droplet in the charging channel should be larger than the charging electrode spacing, to ensure the charging mechanism. The minimum volume of the squeezed droplet with the charging electrode spacing of s would be roughly $s \times w_C \times h$, where w_C is the width of the charging channel and h is the height of the channel. In the sorting channel, the droplet would be in a spherical shape and smaller than the channel height, and its corresponding volume would be $4\pi/3 \times (d_{min}/2)^3$. Thus, the minimum diameter of the droplet d_{min} has to satisfy the following condition, only when $d_{min} < h$:

FIG. 4. Device working zone, droplet size for each flow rate ratio, and photographs for each zone. Flow rate ratio and sorting voltage need to be optimized for stable charging and sorting. (a) The droplet size vs. flow rate ratio. (b) The flow rate ratio vs. minimum sorting voltage. (c) Zone (i) is an optimized area for stable droplet charging and sorting. (d) Zone (ii) is good for charging, but unstable for sorting due to big droplet size. (e) Zone (iii) is not good for charging due to small droplet size.

$$d_{min} = \left(\frac{3sw_ch}{2\pi} \right)^{\frac{1}{3}}. \quad (5)$$

In our device, $d_{max} = \sim 134 \mu\text{m}$ and $d_{min} = \sim 46 \mu\text{m}$ [Fig. 4(a)].

As discussed in our previous work,¹³ the decreasing trend of the droplet size as a function of Q_{ratio} was observed as $r^{-1} \propto Q_{ratio}$, which allowed us to conclude that larger the flow rate ratio, smaller the droplet size [Fig. 4(a)]. Subsequently, we also observed that the sorting behavior was

strongly dependent on the flow rate ratio and the sorting voltage [Fig. 4(b)]; as the flow rate ratio increased, the amplitude of the sorting voltage decreased. The operating point in Fig. 4(b) indicates the working condition for the previous experiments in Figs. 2 and 3. These two results [Figs. 4(a) and 4(b)] come together to support Eq. (3): when the deflection value is fixed to $y=y_{\min}$, smaller droplets need less sorting voltage.

When $Q_{\text{ratio}}=3-6$, the droplet diameter was in the range of $d_{\min}$ and $d_{\max}$ [Zone (i) in Figs. 4(a) and 4(b)]. In this operating range ($d_{\min} < d < d_{\max}$), the droplets were stably charged and sorted [Fig. 4(c)]. When $Q_{\text{ratio}}=2$, the droplet diameter was larger than $d_{\max}$ [Zone (ii) in Figs. 4(a) and 4(b)]. In this range ($d > d_{\max}$), the successfully charged droplets needed a high sorting voltage, but were not stably sorted [Fig. 4(d)]. The center of deflected droplets could not place within the laminar flow of lower stream due to their size ($d=140\text{ }\mu\text{m} > d_{\max}$), which led to unsuccessful droplet sorting. Moreover, the droplet fusion occurred at the sorting junction due to insufficient spacing between adjacent droplets. Once the droplets reached the sorting junction, the droplet spacing decreased due to three branched channels, which was followed by passive droplet fusion.^{17,18} Furthermore, when Q_{ratio} was 7 [Zone (iii) in Figs. 4(a) and 4(b)], the preformed droplets could not cover both electrodes in the charging channel due to their small size ($d=33\text{ }\mu\text{m} < d_{\min}$), which led to unsuccessful droplet charging [Fig. 4(e)].

The critical aspect in this sorting mechanism is the squeezing of the droplet in the narrow channel. The squeezing ensures the droplet to be in contact with the ground electrode while a charge is induced on the water-oil interface when the droplet moves over the insulated charging electrode. When the droplet fails to be in contact with both electrodes at the same time, no charge is induced; therefore, the droplet diameter should be larger than $d_{\min}$ to ensure the charging mechanism. In general, we can expand the operating range ($d_{\min} < d < d_{\max}$) for successful charging and sorting by modifying device geometries. To decrease $d_{\min}$, we can reduce the spacing, the channel width, or the channel height from Eq. (5). To increase $d_{\max}$, we can use wider microfluidic channel which yields larger w_S from Eq. (4).

IV. CONCLUSION

We have presented an on-demand droplet charging and sorting mechanism in a droplet-based microfluidic device. This was accomplished by electrostatic induction on individual droplets and electric deflection of the charged droplets into designated sorting channels. Depending on the polarity on the charging voltage, the droplets could be charged positively or negatively, followed by an automatic real-time electric sorting. We performed the continuous and selective droplet charging and sorting by the pulsed charging voltage. We also studied the behavior of the charged droplets as functions of the sorting voltage and the droplet size: the operational sorting voltage needed to be larger than the minimum sorting voltage to deflect the charged droplets, and the droplet size must be in the range of $d_{\min}$ and $d_{\max}$ for stable droplet charging and sorting. The advantage of our device is the on-demand droplet manipulation mechanism which allows robust control of individual droplets with a positive, a negative, or with no charge. The electrostatic droplet manipulation mechanism opens a plethora of possibilities for further on-chip downstream manipulation of individual droplets.

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