Transport phenomena of immiscible fluids in microchannels

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TRANSPORT PHENOMENA OF IMMISCIBLE
FLUIDS IN MICROCHANNELS

YIN SHUAI

School of Mechanical and Aerospace Engineering

2021

TRANSPORT PHENOMENA OF IMMISCIBLE FLUIDS IN MICROCHANNELS

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School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University in partial fulfillment of the
requirement for the degree of Doctor of Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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27 August 2020

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Associate Professor Wong Teck Neng

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 3 is published as Huang, Y., Yin, S., Chong, W. H., Wong, T. N., & Ooi, K. T. (2019). Precise morphology control and fast merging of a complex multi-emulsion system: the effects of AC electric fields. *Soft matter*, 15(28), 5614-5625. DOI: [10.1039/C9SM00430K](https://doi.org/10.1039/C9SM00430K).

The contributions of the co-authors are as follows:

Huang, Y. and I contributed equally to this paper. A/Prof. Teck Neng Wong initialized the research. I designed and conducted the experiments at the School of Mechanical and Aerospace Engineering with Dr. Yi Huang. Dr. Yi Huang analyzed the data with the help of me and Dr. Yi Huang drafted the manuscript. A/Prof. Teck Neng Wong, Prof. Kim Tiow Ooi Dr. Wen Han Chong and I revised the manuscript.

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26 August 2020

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Yin Shuai

Abstract

Due to the prevalence of miniaturization in the past two decades, microdroplets have been widely applied to the fields of chemistry, biology, and material science. Particularly, microdroplet has recently emerged as an excellent platform for diverse applications because of its incomparable controllability in handling small volumes of fluids. The precise formation of the microdroplet in microfluidic devices has drawn tremendous attention from researchers. Coupled with external control, active droplet formation is proposed to further improve the flexibility of the technique and hence the overall performance of the microfluidic devices.

The electric field has been proven to be an effective active technique in microfluidic devices for precise manipulation of microdroplets. The potentials of complex droplets, specifically oil in water in oil (O/W/O) and water in oil in water (W/O/W) double emulsions, are extended by investigating the effectiveness of AC electric fields on the formation and the manipulation of the two droplet systems. The double-flow-focusing geometry together with the non-contact type of electrodes is adopted to achieve the hydrodynamic generation of the double emulsions under the AC electric field. The results show that the AC electric field is capable of controlling the size of the outer droplet in the O/W/O system hence achieving the control of the inner core droplets. The electric capillary number Ca_E was adopted to analyze the effectiveness of the AC electric field applied at high frequencies, which offered a guideline for practical

applications. Moreover, both the one-step and the two-step merging of the core droplets in the W/O/W droplet system have been achieved within 100 milliseconds, which are by far the fastest merging in double emulsions ever reported.

To reveal the mechanism behind the electric-field-controlled droplet formation, the water in oil (W/O) droplet formation was investigated in a flow-focusing microchannel under AC electric field experimentally and numerically. A three-dimensional numerical model was built combining the Volume of Fraction (VOF) method and the leaky dielectric model, which reveals the droplet formation mechanism under the effects of an electric field. Due to the Maxwell stress induced by the electric field, the sinusoidal waveform electric field induces the oscillation at the liquid interfaces, which accelerates/stimulates the breakup of the disperse phase and thus tunes the droplet size. The phenomena were analyzed by the electric capillary number Ca_E evaluated according to the numerical results. The dominating effect of the pressure difference between the disperse phase and the continuous phase shifts from the initial hydrodynamic pressure pattern to an electric-field-induced one during the evolution of the electric voltage. The numerical results show that the surge in the magnitude of the electric body force tends to stretch the disperse phase at liquid interfaces, which leads to the transition of droplet formation from dripping to jetting under the electric field. This study will lead to a better control strategy for droplet formations with applied electric fields.

In addition, a universal and simple method is developed to actively generate oil in water (O/W) droplet in a Poly(dimethylsiloxane) (PDMS) based microfluidic device by using both DC and AC electric fields to cut a stable layered flow of disperse phase into dispersed droplets in a precise manner. The system owns the feature of ultra-fast response and precise control of O/W droplet generation. The square waveform electric field was proven to be effective in terms of precise cutting and tuning the size of the generated droplet. Controlled by the sinusoidal AC electric fields, the breakup of the disperse phase can be cataloged into three stages, namely, non-breakup, transition, and continuous breakup. The voltage boundaries in between these stages were also located. To demonstrate the generality of the proposed method, the control strategy was applied to four typical oil fluids, all of which had gone through thoughtful tests with success considering different hydrodynamic characteristics. The biggest advantage of the proposed approach is that it removes the necessity of surface treatment for O/W droplet formation in PDMS microchannels, breaking the limits brought by the surface wettability for the first time and rendering itself to be a universal method for O/W droplet active generation with outstanding controllability. Our findings would widen the applications of the PDMS based microchips.

In the end, a novel magnetic Janus particle as a steerable micro-scale suspension was proposed, consisting of a liquid oil compartment and a solidified compartment with magnetic nanoparticles inside. The formation of the Janus droplet in the microfluidic device was studied and hence the Janus particle is fabricated by accurate UV curing of

the magnetic compartment within the Janus droplet. The size and the ratio between the two compartments of the Janus droplet can be controlled by hydrodynamical conditions. A custom-made external magnetic field was applied to steer the Janus droplet. Rapid rotation of the Janus particle under the magnetic field was studied and the relationship between the angular velocity of the Janus particle and the frequency of the applied magnetic field was revealed. The results demonstrate the potential of the magnetic Janus particle for micro-scale vortex generation and substance steerable carrier.

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List of symbols

a	Characteristic length
A	Area of droplet
A_f	Occupied area of dye
b	Length of the electrode area
C_{PDMS}	Capacitance of PDMS gap
Ca_E	Electric capillary number
d	Distance between electrodes
D	Effective diameter
D_{out}	Effective diameter of outer droplet
E	Electric field strength
$\vec{E}$	Electric field
f_b	Breakup frequency of disperse phase
f_c	Electric frequency at low range
f_e	Electric frequency
f_m	Frequency of magnetic field
$\vec{F}_E$	Electric field induced stress
$\vec{F}_{IF}$	Interfacial tension stress
F_E^*	Dimensionless electric body force
H_{ch}	Height of microchannel
$\mathbf{I}$	Identity tensor
P	Pressure

P_c	Pressure of continuous phase
P_d	Pressure of disperse phase
q	Volumetric density of electric charge
Q_{IP}	Volume flow rate of inner phase
Q_{MP}	Volume flow rate of middle phase
Q_{OP}	Volume flow rate of outer phase
R	Radius of core droplet
R_c	Resistance of continuous phase
R_D	Resistance of disperse phase
R_e	Radius of electrode head
t	Time
t^*	Dimensionless time
T_e	Period of AC electric field
$\mathbf{T_M}$	Maxwell stress tensor
T_{DG}	Period of one droplet generation
U	The peak to peak voltage applied on electrodes
U_d	The voltage in disperse phase
U_{cd}	Critical voltage to trigger the breakup of the disperse phase with DC electric field
U_{c1}	Critical voltage to trigger the breakup of the disperse phase with sinusoidal waveform AC electric field
U_{c2}	Critical voltage to trigger the continuous breakup of the disperse phase with sinusoidal waveform AC electric field
U_{Fluids}	Voltage across the disperse phase and the continuous phase

$\vec{v}$	Velocity
V	Real time voltage applied on electrodes
W_{ch}	Width of microchannel
W_C	Width of continuous phase
W_D	Width of disperse phase
W_{ga}	Width of the gap between the electrode and the fluid channel
X_{PDMS}	Capacitive reactance of PDMS gap

Greek Symbols

α_q	Potion of qth fluid in a computational cell
ε	Electric permittivity
ε_{op}	Electric permittivity of outer phase
ε_c	Electric permittivity of continuous phase
γ	Interfacial tension coefficient
ρ	Density
μ	Viscosity
σ	Electric conductivity

Subscripts

C	Continuous phase
D	Disperse phase
IP	Inner phase
MP	Middle phase
OP	Outer phase
E	Electric field

Chapter 1 Introduction

1.1 Background and motivation

The microdroplet is a typical form of multiphase phenomenon composited of immiscible fluids. Due to the unique physical properties and the followed advantages, microdroplet has now become a versatile tool for various applications [1-3]. In materials science, the microdroplet provide flexible choice of materials, normalized and controllable morphology, which can be employed in the synthesis of microparticles [4], microcapsules [5, 6] and other micro structures [7]. Furthermore, microdroplets are excellent microreactors in chemical research [8]. Chemical and biochemical reactions can be conducted in droplets with precise control and much higher efficiency due to the high surface to volume ratio [9]. Moreover, because of the nano or even femto-liter scaled volume, microdroplets can help to downscale the amounts of reagents significantly. More importantly, the microdroplet provides an interface between fluids generating a protection structure for the fluids inside droplets thus—greatly reduce negative impacts or possible contaminations from the outer environment. Nowadays, microfluidic devices have become the irreplaceable tool for microdroplet formation due to its outstanding controllability of hydrodynamics. Moreover, the accessibility for integration of external fields promotes the controllability into a higher level.

The electric field with the merits of fast response and easiness has been proven to be an excellent external energy input for further improvement of the microfluidic devices for aqueous droplet formation [10-12]. However, the dynamics of the electric-field-controlled droplet formation has yet to be fully revealed.

At the present, different forms of microdroplet have been developed to adapt the requirements from multifarious applications. Double emulsion, including the oil in water in oil (O/W/O) type and the water in oil in water (W/O/W) type, is a complex droplet system, where smaller droplets are encapsulated inside a larger droplet forming the typical core-shell structure. This structure provides an extra intermediate phase between the inner droplets and the surrounding phase compared to the single emulsion (simple droplet system). Thus, double emulsion is of high potentials for drug delivery [13, 14], controlled drug release [15] and micro chemical reactions inside [7, 9, 16], all of which are built upon the foundation of precise control over the formation of the abovementioned two types of double emulsions. Therefore, the precise formation strategy of the double emulsion is of high demands and is to be explored. The possibility of the double emulsion in application of micro-reaction should also be furtherly extended and investigated.

Poly(dimethylsiloxane) (PDMS) is a dominant material in the fabrication of microchannels. The related manufacture techniques have been well developed. However, due to its highly hydrophobic nature, an extra surface treatment is required

to the PDMS microchannel for organic microdroplets formation, which always affects the smoothness of microchannel surfaces and thus limits the making the most of controllability of the microfluidic devices. At the present, organic microdroplet has been widely utilized in fields such as microcarrier [14, 17-19], bioscreening [20-22] and analytical chemistry [23-25]. The precise generation of organic droplet has drawn more attention than ever before, however, the research of active formation of the organic droplet is lacking. Therefore, a better formation strategy for oil droplets in PDMS microfluidic devices must be developed, which will minimize the negative effects from the surface treatments and maximize the controllability of the droplet formation. To achieve this goal, the usage of an electric field is crucial.

Janus droplet, due to its feature of functional anisotropy, has been of great interest to researchers. Using the external fields, Janus droplet becomes a steerable micro-scale active suspensions [26] with fascinating perspectives: targeted drug delivery [27], bottom-up synthesis of micro structures [28], artificial chemotactic systems [29], *etc.* Microfluidic devices have the ability to precisely form the Janus droplet with functional compartments, which will further improve the steerability of the active suspension and expand its practical potentials.

1.2 Objectives and scopes

The objective of this study is to improve the controllability of the various types of microdroplets' formation in the microfluidic channel, uncover the dynamics behind

the electric field controlling phenomena and explore the possibility of the microdroplet in practical applications. First, the electric field is to be employed as an active control method to control the formation and manipulation of double emulsion in microfluidic devices. To better understand the active control, the dynamics behind the interaction between the electric field and the flow field has to be studied. Based on the above understanding, the active control method for oil droplet formation is to be proposed and tested. To further expand the scope of this study to include practical application with the microfluidic devices, an efficient formation strategy for steerable magnetic Janus particle is to be explored and its steerability is to be tested.

Therefore, the scope of the current study includes:

- To study the dynamics of oil in water in oil (O/W/O) and water in oil in water (W/O/W) double emulsion formation under alternative current (AC) electric fields in microfluidic channels. To explore relationships between morphologies of the double emulsion and the parameters (such as the voltage magnitude and the frequency) of the electric field. To develop a strategy of precise control on the size and the core number of the O/W/O double emulsion under the electric field. To explore the potential of the electric field for coalescence between/among aqueous inner droplets in W/O/W double emulsion. To uncover applicational potentials of the electric field on W/O/W double emulsion.

- To numerically investigate the water in oil droplet formation under AC electric fields in flow-focusing microchannels. To develop a proper numerical model to interpret the interaction between the hydrodynamics and the electric field. To explore the impacts of the electric fields with different voltages and frequencies on the droplet formation.
- To develop an active strategy for the oil droplet generation inside the microchannel with the electric field. To explore the impact of the DC and AC electric fields on the oil droplet formation and develop a universal approach to generate the oil droplet precisely. To verify the applicability of the strategy with different oil fluids.
- To develop a microfluidic system for magnetically responsive Janus droplet. To study the formation process of the Janus droplet with one solidified segment which carries magnetic nanoparticles inside. To explore the controllability of the external magnetic field on the steering of the Janus droplet and explore applicational potentials of it.

Chapter 2 Literature Review

2.1 Microdroplet formation in microchannel

The emergence and the prosperity of microfluidics in the past decade, in particular droplet microfluidics, have created novel approaches in researches such as the micro-reactors [9, 16], material synthesis [30], and drug delivery [31]. Microdroplets can be generated by many methods. Among them, microfluidic methods (Figure 2-1) afford irreplaceable fine control of the formation of droplets [32-34]. In some high-demanding situations, the on-demand drops can only be generated by delicate assignment of fluids supply, therefore the microfluidic device is widely used in drops formation and correlational studies due to its high level of controllability on tuning droplet formation.

Figure 2-1 Droplet formation in microchannel[32]

2.1.1 Regimes and geometries of droplet formation

Droplet generation originates from fluid instabilities. Generally, in microfluidic methods, a drop comes from the introduction of one fluid (dispersed fluid) into another one (continuous fluid), both of which are immiscible to each other. It happens in four regimes: squeezing, dripping, jetting and thread forming [32] (Figure 2-2). The

squeezing regime exhibits quasi-static mechanisms [35] because of the channel confinement. The other three regimes arise from the capillary instability. In other three regimes, the interfacial tension forces aim at minimizing the interfacial area while the viscous and inertial forces seek to deform the liquid interfaces. The competition of these forces determines the specific formation regime.

Figure 2-2 Four regimes in the formation of droplet: (a) Squeezing; (b) Dripping, (c) Jetting; (d) Thread forming. [36]

Capillary number (Ca) is an important parameter in this section influencing which form appears. Ca is determined by flow geometrical parameters and fluids properties. The channel confinement results in squeezing regime with a small value of Ca , causes the continuous fluid to squeeze the dispersed fluid till the breakup. With a larger value of Ca , interaction among interfacial tension forces, viscous and inertial forces on dispersed fluid determines the specific breakup of the other three regimes of droplet formation under a certain set of conditions (Figure 2-3).

$$Ca = \frac{\mu v}{\gamma} \quad (2.1)$$

Where:

μ - Dynamic viscosity of the fluid

v - Velocity of the fluid

γ - Interfacial or surface tension between the two fluid phases

Figure 2-3 The relationship within the formation forms, the Ca number and the flow rate [36]

In the above formation forms, the droplets size is related to the interfacial tension, viscosity of fluids and the inertial forces. Hence the common dimensionless parameters to characterize the relationship between those forces, except for Ca number, are the Weber number and Reynolds number. Re number is the ratio between the inertia force and viscous force. While the We number shows the relative importance of inertia force and interfacial tension. Weber number can be written as:

$$We = \frac{\rho v^2 l}{\gamma} \quad (2.2)$$

Where:

ρ – Density of the fluid

l – Characteristic length

Another important dimensionless number is Reynolds number Re :

$$Re = \frac{\rho vl}{\mu}$$

Re represents the ratio of inertial forces to viscous forces within a fluid.

The micro-scale makes the inertial effect ignorable, thus the Ca number is the most essential characterized number in microfluidic droplet research.

Three kinds of basic microchannel geometries have been proposed for droplets formation in microfluidics channel. They are T-junction [35, 37], flow focusing [36, 38], and co-flowing [39, 40] (Figure 2-4). All of them are able to produce monodisperse droplets. Each of them has its individual characteristics. These three droplets formation geometries generate droplets by triggering instability at the interface between fluids.

In T-junction geometry (Figure 2-4 (a)), the dispersed and continuous phases are fed orthogonally. Because of its simple structure and the ability to form monodisperse droplets, the T-junction is widely used. In co-flow geometry (Figure 2-4 (b)), the dispersed and continuous phase flow in parallel directions. This geometry is first introduced by Umbanhowar [41].

Figure 2-4 Different channel geometries for droplet formation (a)T-junction; (b)Co-flowing; (c)Flow-focusing. [42]

Ganan-Calvo [43] produce the monodisperse droplet in a flow focusing geometry (Figure 2-4 (c)) first. In flow-focusing geometry, the dispersed and continuous fluids meet at a junction, and then the fluids pass through a contraction process. Commonly, the flow-focusing is more reliable for size controlling of droplets [1]. There are many variations of the flow-focusing geometry merging throughout the years. The typical variation of the geometry is the use of orifice at the junction. Figure 2-5 illustrates the sketch of the flow-focusing geometry with or without orifice. Because of the orifice, the upstream flow reaches a higher velocity and the fluid is squeezed at the orifice, thus the droplets generated can be smaller. This is an effective method to obtain smaller droplets without the need to change other geometry parameters, which is important in some applications with limited space of the microchannel.

Figure 2-5 The flow-focusing geometries without orifice and with orifice [44].

Above-mentioned geometries are 2D designed structures. There are various 3D-designed microchannels emerging in recent years. In order to achieve higher throughput or enhance the stability of droplet formation, 3D microchannels have been used in microfluidics. Step structure is used for generation of microdroplets [45, 46]. By using the shape change of channel at the step, the capillary pressure changes and the interfacial tension drives the droplet generation. Besides, non-planar array [47, 48] of microchannels was made to achieve high throughput of droplets. Figure 2-6 shows the step structure for droplet formation. However, these 3D structures make the fabrication process of the microchannel complicated.

Figure 2-6 The non-planar microchannel for droplet formation [47].

Using the flow rates or geometries to control the size or structure of double emulsion is usually limited especially considering the diverse properties of the fluids employed. Researchers find the vulnerability of hydrodynamic control over the droplet size or the core-shell structure [49, 50]. Therefore, the active methods in droplets formation start to be applied in droplet formation. The active method refers to the use of external disturbance to tune the flow conditions and thus add another level of controllability in droplets formation. Usually, the active methods have fast response time on tuning of droplets and work beyond as a tuning tool in some extreme conditions, such as breaking the dispersed phase with high viscosity or high interface tension [42].

2.1.2 Active droplet formation methods

In the passive method for droplet formation, viscous and inertial forces tend to deform the liquid interfaces while the interfacial tension force acts against it. Therefore, the competition of these forces dominates the formation of droplets, while for the case of active droplet formation with the external energy inputs, the extra forces are introduced into the system endowing the systems with better customizability on droplet formation. Many artful techniques have been introduced in active control of droplets formation. Electrodynamics [11, 51], thermodynamics [52, 53], and magnetodynamics [54] are adopted into this research by using sophisticated device to generate electric, thermal, magnetic fields around the microfluidics device respectively, which provide additional degree of control on droplet formations.

The surface acoustic wave (SAW) was also used in droplet formation control. Schmid et al. [55] demonstrated the drop formation in a flow-focusing geometry with the effect of a surface acoustic wave actuation located at the junction. With the SAW works, the droplet length decreases when the signal power of SAW increases as illustrated in Figure 2-7 (a). The droplet formation impacted by temperature field was also reported [52]. A microheater was embedded at the junction of the flow-focusing structure. By activating the heater, the size of droplet can be changed because the interfacial tension varies. The local temperature changes the interfacial tension between the two fluids and thus the size of the droplets (Figure 2-7 (b)). Except for temperature field, heating a point in flow field is also an active method for controlling. The active control of droplet formation by localized heating from a laser was proposed [56]. The localized heating generated a large temperature gradient in the fluid and thus induced an extra flow which influenced the interface (Figure 2-7 (c)).

Figure 2-7 The droplet formation under the control from (a) surface acoustic wave [55], (b) temperature field [52] and (c) point laser heating [56].

The DC [9, 12, 57] and the AC [10, 11, 58] electric fields are proven to be capable of controlling the aqueous droplet formation and coalescence due to the electric field induces Maxwell stress at the liquid interfaces. However, the electric field tuned oil droplet formation is yet to be reported. Figure 2-8 shows a setup for droplet formation under DC electric field. The ITO (Indium tin oxide) electrodes generate the electric field across the microchannels. In recent years, non-contact type of electrode has been applied in droplet formation control with AC and DC electric field. The results of these works show enormous potential of electric field in droplet tuning due to fast response time and high efficiency [11, 50].

Figure 2-8 The electrodes setup for active controlling droplet formation. The electrodes are made from ITO (Indium tin oxide) [12].

Generally, upon application of the high voltage to the electrode, electric field is generated across the area in between the pair of the electrodes where the fluidic sample is constrained by the channel. Induced free and bound charges accumulate at the liquid interfaces. Thus, the interaction between the charges and the electric field perturbs the interface. The interaction results from the Maxwell stress which can be defined as:

$$\mathbf{T}_M = \varepsilon(\vec{E}\vec{E} - \frac{1}{2}\vec{E} \cdot \vec{E}\mathbf{I}) \quad (2.3)$$

Where ε is the electric permittivity, $\vec{E}$ represents the electric field, and $\mathbf{I}$ is the identity tensor.

To describe the electric field and its interaction with the flow field, the leaky dielectric model [59, 60] is proposed for poorly conducting liquids under electric field. Under the assumption of this model, the redistribution of free charge is instantaneous

when compared to the fluid mechanics time scale. Therefore, using the continuity of the electric current equation at the interface:

$$\frac{\partial q}{\partial t} + \nabla \cdot (\sigma \vec{E}) = 0 \quad (2.4)$$

we can obtain:

$$\nabla \cdot (\sigma \vec{E}) = 0 \quad (2.5)$$

Where q denotes the volumetric density of electric charge. σ is the electrical conductivity and t is time. To characterize the relative importance between the Maxwell stress and the interfacial tension in the flow field, electric capillary number (Ca_E) is employed:

$$Ca_E = \frac{\varepsilon E^2 a}{\gamma} \quad (2.6)$$

Where E is the electric field strength. γ is the interfacial tension coefficient. a is the characteristic length. The phenomena of the droplet formation under the electric field are always related to the level of Ca_E .

2.1.3 Numerical investigations on droplet formation

The observation of microdroplets formation is limited under normal microscope conditions. The analysis of the formation is difficult with only the experimental results because of the lack in multi-dimensional data of the interfaces motion, the velocity field, the pressure distribution *etc.*, which are crucial for understanding the dynamics of droplet formation but hard to obtain in experiments.

Figure 2-9 The comparison between the experimental and numerical droplet formation results [61].

The droplets formation in microfluidics is a form of multi-phase flow. During the formation, the unsteady fluid-fluid interfaces made the analysis challenging. The interaction within fluids or between the fluids and solids has to be understanding for explaining the experimental phenomena and practical applications. At present, the development of high-speed computer enables the precise simulation of the microdroplet formation as a complement of experiments. This helps to reveal the mechanism of the breakups of droplets. Numerical investigation of droplets formations has been studied by many groups. The Boltzmann method [61-65] (Figure 2-9), multi-phase level-set method [66, 67], phase field [68, 69] and Volume of Fraction (VOF) method [70, 71] are the common models for interface tracing in simulations of the droplet formation.

The numerical research of the droplet formation under external field is reported as well [72, 73]. The droplet formation under DC electric field can be predicted in numerical models (Figure 2-10). The interaction of the electric field and the electric charges at the fluid interfaces upset the dynamic equilibrium between the interfacial tension force, inertia force and the viscous force and thus affect the droplet formation greatly in the size and the formation regimes [73].

Figure 2-10 The numerical simulation of the droplet formation process (a) without and (b) with the DC electric field [73].

2.2 Double emulsion formation in microchannels and its applications

Double emulsion is the droplet with one or more smaller droplets inside. A double emulsion is defined as an emulsion in an emulsion. Because of its core-shell structure, stronger protection of inner phase during delivery has been proved [74]. Meanwhile,

since techniques of controlled release and mix of chemicals in the inner phase become reality, double (or multiple) emulsion has been applied in the industries [30]. In recent years, microfluidic devices, as the novel tool for double emulsion generation have shown great potential to address the challenges in the double emulsion formation, which offers great control over the emulsification and the quantity control.

With the accurate control of the size, structure and release in microfluidic devices, double emulsion has been proposed in myriad applications due to its core-shell structure, which is highly desirable for material transport and protection [13]. Figure 2-11 demonstrates the structure of double emulsion [75]. The green part, blue part and the grey part in Figure 2-11 (a) refer to the inner droplet, outer droplet and the continuous phase respectively. Generally, double emulsions may be either of the water-in-oil-in-water (W/O/W) type or oil-in-water-in-oil (O/W/O) type.

Figure 2-11 Double emulsion: (a) The schematic diagram for the double emulsion. (b) The double emulsion formed in microchannel [75].

2.2.1 Formation of double emulsion

Figure 2-12 demonstrates the typical structure of a coaxial nozzle device [76-78] for double emulsion formation. The inner phase and middle phase are supplied into the device in parallel coaxial capillaries, while the outer phase is supplied in opposite direction and the fluids meet at the entrance of a narrow orifice, breaking up of the immiscible fluid interface between the inner and middle phase form the double emulsion (Figure 2-12). However, the 3D structure makes it difficult to fabricate and reduce its durability.

Figure 2-12 The double emulsion formation in coaxial nozzle device [78].

Two hierarchical flow-focusing [79] and T-junction [80] geometries have been proposed to form double emulsion (Figure 2-13). Besides, this hierarchical structure can be used in higher-order multiple emulsion (e.g. triple emulsion) formation by adding more droplets formation geometries at downstream (flow-focusing and T-junction geometry). With delicate structure, these devices can offer limited control over the size of the inner and outer droplets and the number of the inner droplets.

Figure 2-13 The hierarchical flow-focusing geometry for double emulsion formation. The double emulsion is formed at the second junction [81].

As shown in Figure 2-13, formation of the double emulsion in the microchannel using sequential breakup through two flow-focusing geometries. The inner droplets and the outer droplets form at the first junction and the second junction, respectively. The structure owns a brilliant controllability of double emulsion since the two junctions enable the separate control of the inner droplet and the outer droplet of the double emulsion. Using the photolithography, the mass production of this 2D is feasible and the active generation techniques can be easily integrated with better controllability.

2.2.2 Applications of double emulsions

Every phase of double emulsion can be a carrier of reagents, double emulsions present many attractive possibilities due to the core-shell structure. The field of human pharmaceuticals [82-84], the materials [85, 86] (Figure 2-14), the biology [87], and the food [88] are the major areas for applications. Besides, double emulsion can also be used to generate Janus particle [89] or porous particle [85, 90].

Figure 2-14 The material synthesis inside droplet. (a) Before and (b) after the hydroxyapatite in the inner drops of the double emulsion [85].

Using double emulsion as an excellent carrier or container for substances has been reported [15, 91-93], which greatly promotes the development of micro-scale drug delivery. For micro-reaction application, using electric field to trigger the coalescence of droplets inside the double emulsion as a container has been proposed [7, 9, 16]. Figure 2-15 shows the double emulsion triggered coalescence of droplet inside the double emulsion, the coalescence of two cores inside double emulsion requires at least 10 seconds. All these applications require fine control of double emulsion formation with high throughput. Therefore, the techniques of double emulsion formation with precise control and high throughput become the one that needs to be improved.

Figure 2-15 Electrocoalescence in double emulsion[9].

2.3 Janus micro droplet/particle formation and its applications

Janus microdroplet is another kind of multicompartamental droplets, which possess two parts with physically and chemically distinct segments. Due to its feature of functional anisotropy, the Janus droplet can be utilized for various applications, such as chemical, biological sensing, drug delivery and material synthesis [94]. Figure 2-16 illustrates the formation of Janus droplet in microfluidic devices and the Janus droplet collected outside of the chips.

The microfluidic dynamics for forming the Janus droplet are similar to that of the homogeneous ones. In most reported works, to form the Janus droplet, two separate streams are coflowed through the same channel of the microfluidic device before the droplet formation geometries (co-flowing, flow focusing, T-junction). To successfully form the Janus droplet, the two disperse phases are required to be miscible and the interfacial tension between the fluids need to be within a certain range. Otherwise the

two “heads” of the Janus droplet will not adhere to each other and thus producing individual droplets [89].

Commonly, the Janus particle comes from solidifying the Janus droplet. After formation, the Janus droplet can be solidified through various methods [94]. The ultraviolet light irradiation of Janus droplet with monomers and photo initiator is widely used for solidification [95, 96]. Besides, the polymerization reaction is another method for solidification of Janus droplets [97, 98].

Figure 2-16 Janus particles : (a) Janus droplet formation inside microchannels [98] and (b) the Janus particles collected [99].

2.3.1 Application of the Janus droplet/particles

Various anisotropies have given the Janus droplet/particle a wide variety of applications. Color anisotropy endows the visual differentiation to the Janus droplets, which extends the microdroplets into the applications such as displays and labelling for bioassays [100-102]. The electrical anisotropy and magnetic anisotropy render the Janus droplet to be the carrier with controllable movement for substance delivery [103,

104]. Degradable anisotropy of the compartments enables the production of heteromorphic particles [105-107].

Using the external fields, it is now possible to fabricate artificial micro-scale Janus particles capable of self-propelling in the fluids [108, 109] (Figure 2-17). A number of works have reported magnetic and electric responsive Janus particles [110-112]. Commonly, the metal nanoparticles are dispersed inside one side or coated at the one side's surface of the Janus particle to be magnetically or electrically responsive. Such technique is essential in chemical and biological systems for accurate substance delivery. The transportation of the Janus particle with active steering is becoming the focus to the researchers.

Figure 2-17 The trajectory of the Janus particles under feedback control electric field. (a) The letters “UT” and (b) a cherry blossom flower [108].

2.4 Fabrication of microchannels

With the advanced development of semiconductor fabrication technology, the silicon-based fabrication dominant the micro scale manufacture. For microfluidic research, this technology provides the methods to fabricate the microchannels. PDMS

and soft lithography techniques [113] are applied commonly in microfluidic research among the world. Whiteside's group at Harvard University invented a procedure to bond two PDMS surface [114-116] for complex microchannel structures. The fabrication of microchannel is based on soft lithography, which has lower cost than conventional photolithography. The poly (dimethylsiloxane) (PDMS) is a low-cost and high light transmission material, which is widely used in micro-scale structure prototyping. Figure 2-18 describes the main procedures of PDMS fabrication based on soft lithography[117].

Figure 2-18 The photolithography process to fabricate the microchannel [117].

2.5 Surface treatment

For the formation of the water in oil droplets and the oil in water droplets, the requirements of wetting property of channel walls are different. Surface treatment of channel walls of one junction is necessary. Polydimethylsiloxane is a dominant polymer in the fabrication of the microfluidic devices. However, because the PDMS microchannel is highly hydrophobic, the oil in water droplets formation in PDMS channel needs a treatment to the hydrophilic channel walls so that the contact angle of oil on wall can be increased for successful formation of oil droplets. The patterning of wettability within enclosed microchannel has been challenging in the past years for the oil droplet formation.

At present, the graft polymerization of acrylic acid, acrylamide, 2-hydroxyethylacrylate and poly(ethylene glycol) monomethoxyl acrylate (PEG) are successful options for surface treatment [118]. The grafted surfaces have a decreased contact angle for water. The deposition of polyvinyl alcohol (PVA) is also proved to be an effective and low-cost surface treatment method for hydrophilic surface. This method is relatively simple, stable with respect to surfactants [119]. Figure 2-19 shows the performances of the coating of PVA. In PDMS microchannels for double emulsion generation, hydrophilic channel surface is essential to the O/W droplet formation and thus the quality of the treatment directly affects the stability of double emulsion generation. Therefore, the surface treatment brings extra workload and unsmooth channel walls to the oil droplet formation in PDMS channels.

Figure 2-19 The comparison between the PDMS channel (a) untreated and (b) treated with the PVA coating [119]

2.6 Surfactants in droplet formation

Surfactant plays an essential role in droplet-based microfluidic [120-122]. Taking advantage of proper surfactant is vital for droplet generation. Usually, surfactants are used to assist droplets formation, tune the droplet size and strengthen the stability of droplets [123, 124]. It is a basic tool to adjust the property of fluid interfaces. Surfactant is a blend of surface-active agent which contain both hydrophobic groups and hydrophilic groups. This property leads to the stabilization of droplet interfaces.

In addition, for tuning the droplet formation, the heterogeneous distribution of surfactants at the interface results in a force acting against the fluid flow, which is so-called Marangoni's effect. Because of this effect, when the fluid is breaking into drops, surfactant moves to the neck of the fluids, which slows down the pinch-off process, so the droplets generated will be different from that in the absence of surfactant.

2.7 Summary

Microdroplets have become a fundamental structure in the research of materials synthesis, micro-reactor, drug delivery, etc. Through the use of microfluidics, single-droplet level control has become feasible. DC and AC electric field coupled with the microchannels have been used in tuning droplet formation.

Double emulsion attracted intense interest due to its unique “shell” structure. Thus, the requirement of precise control on the formation of double emulsion is crucial. Electric field has been proven to tune the formation of single emulsion droplets and trigger the coalescence of droplets. The integration of electric field with microfluidic device is to be explored to optimize the double emulsion formation and the manipulation of micro-reaction inside double emulsion.

The dynamics of droplet formation under AC electric field has yet to be fully investigated. The numerical and experimental research on it is insufficient, which is to be studied to understand the interaction between the AC electric field and the droplet formation.

Currently, oil droplet formation in microchannels, has not shared the benefits from the electric field coupling formation. The study on the active formation for the oil droplet is insufficient. Besides, the requirement of the wettability of the channel wall limits the development of it. Therefore, an oil droplet formation strategy aiming for better controllability and fewer restrictions is to be explored.

Janus droplets, depending upon their functional anisotropy, open the possibilities for various applications. The precise controllability on the Janus droplet formation inside the microfluidic devices will help to turn the Janus droplet or particle into a steerable micro-scale suspension, which has enormous potentials in the chemical and biological applications.

Chapter 3 Precise Control and Fast Merging of Double Emulsions under Electric Field [125]

3.1 Introduction

The emerging and prosperity of microfluidics during the past decade [126-131], in particular droplet microfluidics [11, 132-136], have created novel approaches for the fundamental research such as the materials synthesis [137-139], micro-reactor [140-142], drug delivery [143, 144], *etc.*, and shade the light to practical applications, for instances food industries [145-147], fluidic optics [148-151], and pharmaceuticals [152-154]. Among them, the complex droplets, specifically double emulsions [151, 155-157] have attracted intense research interest due to their unique “core-shell” structure which brings tremendous potentials in crucial applications of cell encapsulation at single-cell resolution [158-160], particle synthesis with complex functionalities [161-164], and controlled drug releasing [154-156, 165], all of which are built upon the foundation of precise control and on-demand manipulation of the “core-shell” structures. Comparing with other traditional methods of synthesizing the double emulsions, microfluidic platform shines with the compelling advantages that controlling and manipulation at single-droplet level are feasible, the integration of external fields is readily accessible, and the niche scale meets the requirements rising from bioengineering where typical scale of cells lies in microns [131, 158, 166]. To utilize the advantage of microfluidic platform, a microchip is adopted with a

double-flow-focusing junction laying in a hierarchical manner, which renders itself with flexible controls [11, 35, 51, 143]. To achieve a fast response and finally reach the target of on-demand manipulation [11], the alternating current (AC) electric fields is employed to tune the generation of double emulsions and trigger the merging of inner core droplets (cores for short), which is critical for applications of chemical reactions, drug deliveries, *etc* [167, 168]. Four non-contact type of electrodes imbedded in the microchip are designed to apply the electric field. The electrodes are designed and fabricated intently to avoid direct contact with the samples so that challenges of sample contamination can be overcome.

In this chapter a systematical investigation of the effectiveness of the AC electric field (both the peak-to-peak voltage U and frequency f_e) and the hydrodynamic conditions to the formation of the oil/ water/ oil (O/W/O) double emulsions was conducted. The results prove that the AC electric field is effective in controlling the size of the outer droplet and hence, the number of the cores encapsulated. Moreover, the functionality of AC electric fields in manipulation of water/ oil/ water (W/O/W) double emulsions is explored. The AC electric field is capable of triggering the merging of the inner cores in experiments. To further clarify our concept, the W/O/W emulsions with two distinct types of inner cores are generated, one of which contains the fluorescent dye while the other does not. Merging of the cores is successfully triggered by applying the AC electric field and captured under fluorescent microscopy configuration. Currently, the tuning of the number of inner cores ranging from 5 cores to single core

precisely is achieved with presence of the AC electric field. Furthermore, one-step (two-core) and two-step (triple-core) merging are implemented with the electric field. This work provides a platform of generating and manipulations of double emulsions with great accuracy and flexibility, and reveals the rich physics of interfacial phenomena, which holds grave importance to applications of drug deliveries, micro-reactions, *etc.*

3.2 Experimental setup

The experimental setup is shown in Figure 3-1. The microchannel chip is placed on the microscope platform, the experimental phenomenon is observed under an inverted microscope (Leica DM ILM) and recorded by a high-speed camera (Phantom V611, shutter speed up to 100000 FPS). The record data can be replayed and stored by the computer. The high-precision syringe pump system (Centoni neMESYS) is connected to the chip to manage the injection flow rates of each fluid, which can be controlled by the computer. The waste fluid comes from the microchannel is collected by a waste beaker. In this work, the flow rate of the inner phase liquid, Q_{IP} , is set at 2,4,6,8 $\mu\text{L/h}$. The flow rates of the middle phase (Q_{MP}) and the outer phase (Q_{OP}) are greater than the Q_{IP} . Four flow rates are chosen for the middle phase (20,30,40,50 $\mu\text{L/h}$) and four flow rates are chosen for the outer phase (160,180,200,220 $\mu\text{L/h}$). The microchannel chip was fabricated with soft-lithography technique. The Poly(dimethylsiloxane) (PDMS, Dow Corning Co. SYLGARD® 184) microchannels need to be bonded to a glass slide (Corning, 75×50×1 mm) with thin PDMS coating

to form the channels. The bonding process takes advantage of the oxygen plasma cleaner (Harrick Plasma, PDC-32G). The master of the structure is made by SU-8 (SU-8 3050, Micro-Chem Co.).

Figure 3-1 The experimental setup.

The double-flow-focusing geometry is arranged in the hierarchy manner to generate the double emulsion. The geometrical information is shown in Figure 3-2. Where $W_{ch}=100\ \mu\text{m}$, $W_{ch2}=300\ \mu\text{m}$ and $W_{ga}=50\ \mu\text{m}$.

Figure 3-2 The geometry of the microchannel.

Four inlets are prepared for delivering the samples which creates various fluidic systems (O/W/O and W/O/W). Four non-contact types of electrodes are imbedded at the second flow focusing junction where the double emulsion is formed as shown in Figure 3-3 (a) and the enlarged view in Figure 3-3 (b). For investigation of the functionality of the AC electric field, two types of electric fields are implemented, one in the tangential direction where two of the electrodes downstream are connected to the high voltage while the other two are grounded (Figure 3-3 (c), configuration 1), the other in the normal direction where the two electrodes at one side is applied high voltage so that the direction of the electric field is normal to the flow direction of the outlet (Figure 3-3 (d), configuration 2).

Figure 3-3 Schematics of the microchannel and the configurations for applying the electric fields. (a) 3D illustration of the microchannel, (b) enlarged view at the location where the four electrodes are imbedded and the double emulsion is generated, (c) and (d) are the illustration for the tangentially (configuration 1) and normally (configuration 2) applied electric fields respectively

3.2.1 *External electric field*

The external electric field is implemented by four electrodes imposed inside the PDMS chip. Every electrode has two wire terminals at outside (Figure 3-3). The indium alloy fills the electrode channel to fabricate the main part of the electrode. The electrode channels are within the same plane with the fluid channels, but they are not in contact with the fluid channels. The indium alloy is connected with a high voltage supply source later. There are 4 electrodes located around the second junction in the chip. Anyone of the electrodes can be connected with either the high voltage supply source or the ground. The high voltage supply source consists of a waveform generator (Agilent 33500 B) and a high voltage amplifier (Trek 5/80). The waveform generator is able to generate the on-demand sinusoidal electric signal with specific voltage amplitude and frequency, and this signal is amplified to reach required amplitude through the voltage amplifier. The amplified signal will be delivered to the electrodes connected. Thus, this external electric field setup enables us to apply AC electric field around the second junction of the microchannel. Moreover, the direction and distribution of the electric field can be changed by selecting the certain electrodes to connect with voltage supply source. In experiments, the applied electric signal is sinusoidal waves and the maximum voltage (U) ranges from 0 to 2.5 kV (All the following “voltage” are referring to the maximum voltage of the AC signal). The frequency (f_e) varies within in the range of 0 Hz to 1.25 kHz.

3.2.2 *Surface treatment*

Long term hydrophilic stability and proper thickness of the hydrophilic coating on PDMS channel are important for reliable production of Oil in Water droplets. In the experiments, after oxygen plasma treatment for bonding, the surfaces of PDMS chip has an increase of hydrophilicity due to oxidation of surface siloxane groups to silanols. This hydrophilicity cannot last long time due to the reorientation of the polar groups. Thus, a surface treatment process at specific position of microchannel is necessary for producing the double emulsion.

In the process of surface treatment, a uniform grafted surface is necessary for stable formation of drops. In our experiments, the benzophenone acted as a photo-initiator and was diluted in acetone. This solution was firstly injected into the microchannel. Next step was loading the acrylic acid in water solution into the channel and treated it with UV light for 2-3 minutes. This method is efficient and able to bring a durable surface hydrophilic transition to the PDMS channel.

3.2.3 *Materials*

To generate the O/W/O double emulsions, Mineral oil with 0.3 wt% Span 80 is prepared as the inner phase, Deionized (DI) water with 65wt% Glycerol as the middle phase, and Mineral oil with 5 wt% Span 80 as the outer phase. For generation of the W/O/W double emulsions, DI water with 2 wt% Tween 20 is used as the inner phase, Mineral oil with 0.3 wt% Span 80 as the middle phase, DI water with 70 wt%

Glycerol, 0.3 wt% SDS as the outer phase. For demonstration of merging two different inner droplets, DI water with 2 wt% Tween 20 and 4 mmol/L Rhodamine 6G is adopted as the other inner phase. All the chemicals are purchased from Sigma-Aldrich unless specifically indicated. The properties of fluid can be seen in Appendix A.

3.3 AC electric control on the formation of O/W/O double emulsions

3.3.1 *Effect of the tangential AC electric field on formation of O/W/O double emulsions*

In this section, AC electric fields are applied at the tangential direction (Figure 3-2 (c), configuration 1) where the electric field strength E can be expressed as $E = 0.5 \cdot U \sin(2\pi f_e t)/d$ with U being the maximum voltage of the electric field (peak to peak value), f_e the frequency of the field and d the distance between the two electrodes. The results are cataloged into two groups by the applied frequency f_e : the relatively low range which matches that of the formation frequency of the core droplet (defined as f_c , $f_c < 40$ Hz) and the relatively high range (250 Hz~1.25 kHz) where the electric field shows stronger influence. For each of the catalog, the influence of the AC field (both the voltage U and frequency f_e) on the generation of the O/W/O double emulsions shall be investigated.

Figure 3-4 Formation of the inner droplets and the double emulsion in the microchannel.

The core droplets are generated at the first flow focusing junction, and then the core droplet flow into the second flow focusing junction as encapsulated by the middle phase (Figure 3-4). As the middle phase accumulates at the tip, more core droplets are being encapsulated (Figure 3-5 (a)-(1), $t=107$ ms). Next the middle phase is pushed downstream by the outer phase (Figure 3-5 (a)-(1), $t=167$ ms) which follows by the final breakup procedure where the double emulsion is generated ($t=178$ ms). The whole process is balanced by the viscous stress and interfacial tension. The generation procedure is tuned by applying one AC electric field (Figure 3-5 (a)-(2)).

The middle phase is thinned by the electric field (Figure 3-5 (a)-(2), $t=0$ ms and $t=5$ ms), the outer droplet is obviously deformed by the electric field (Figure 3-5 (a)-(2), $t=22$ ms), the duration of the whole formation process is reduced from 178 ms to 28 ms, and the size of the outer droplet is significantly reduced that the original 5-core O/W/O double emulsions (Figure 3-5 (a)-(1)) become the single or double-core

emulsions (Figure 3-5 (a)-(2)). The results prove the effectiveness of the AC electric field on tuning the generation of O/W/O double emulsions.

a. Formation process of O/W/O double emulsions

b. Effect of volt. under low freq.

c. Dia. Vs. volt. at low freq.

Figure 3-5 Effect of the tangential AC electric field on formation of O/W/O double emulsions. (a) Time evolution of generation process of O/W/O double emulsions for both with (1) and without (2) electric fields; (b) voltage tuned formation with a constant and relatively low frequency; (c) dependency of the effective diameter of the outer droplet on the applied voltage while the frequency is fixed at a relatively low value; (a) and (b) are captured under constant flow rate ratio of $Q_{IP}:Q_{MP}:Q_{OP}=4:30:200 \mu\text{L/h}$. The scale bars indicate $100 \mu\text{m}$.

To continue a systematical investigation of the AC electric, the influence of U under the relatively low frequency f_e (Figure 3-5 (b) and (c)) is firstly explored. The frequency f_e is chosen to match that of the production frequency of the core droplets f_c . The details of the frequency matching phenomena will be discussed in the § 3.6 Discussion section. The applied voltage is gradually increased from 0 V till 2 kV and observe the number of the cores reduces from 5 to 1 due to the reduction of the outer

droplet. When the voltage U reaches 1.1 kV (Figure 3-5 (b)), the number of the cores is limited to one. The size of the outer droplet can be further decreased by enhancing the voltage U which, however, leads to the electro spray making the system unstable ($U=1.5$ and 2 kV in Figure 3-5 (b)). The dependence of the effective diameter of the outer droplet D_{out} on the applied voltage U is shown in Figure 3-5 (c), when the frequency f_e is kept relatively low. A monotonically decreasing trend for various flow rate conditions in Figure 3-5 (c) interprets that a strong electric field applied in the tangential configuration promotes the interfacial instability, lowers the interfacial tension, and hence, reduces the size of the outer droplet, which explains the control mechanism of the AC electric field to the generation of O/W/O double emulsions.

The electric field is applied with various frequencies within low range while the voltage is kept at 800 V, as shown in Figure 3-6 (a) and (b). The results show that increasing the frequency f_e is also capable of reducing the size of the outer droplet and controlling the number of the cores. Increased frequency disturbs the interface between the middle phase and outer phase more frequently leading to an early breakup of the outer droplet. The dependency of the size of the outer droplet D_{out} on the low frequency f_e (Figure 3-6 (b)) also demonstrates a decreasing trend. Compared to the voltage control approach (Figure 3-5 (b) and (c)), the frequency control is not as strong that no stable single core formation is achieved.

Figure 3-6 Double emulsion formation under the tangential AC electric field: (d) the effect of the frequency within a relatively low range; (e) effective diameter of the outer droplet versus the low frequency applied; (f) voltage tuned double emulsion formation with a relatively high frequency; (g) effective diameter of the outer droplet versus the applied voltage while the frequency is kept relatively high. (a) and (c) are captured under constant flow rate ratio of $Q_{IP}:Q_{MP}:Q_{OP}=4:30:200\text{ }\mu\text{L/h}$. The scale bars indicate $100\text{ }\mu\text{m}$.

Next, the frequency f_e is increased and explore the influence of the applied voltage U .

When the frequency f_e increases, the current feed is growing significantly with the enhancing of the applied voltage U . Similar shrinkage of the outer droplet (Figure 3-6 (c)) can be seen and the decreasing trend as well (Figure 3-6 (d)). When the frequency f_e is high, we do observe obvious effect of the electric field. By adjusting the voltage from 500 V to 750 V (Figure 3-6 (c)), the number of the core reduces from 4 to 1 or 2.

A further increased voltage can easily trigger the electro spraying leading to an

unstable system, which makes the precise control of the core number slightly difficult than the scenario shown in Figure 3-5 (b).

More experimental data of effects of the tangential AC electric field on formation of double emulsion can be found in Appendix A.

3.3.2 Effect of the normal AC electric field on formation of O/W/O double emulsions

Figure 3-7 Effect of normal AC electric field with low frequencies on the formation of the O/W/O double emulsions. (a) Influence of the voltage on the formation of O/W/O double emulsions, where electric field is applied in normal configuration with a relatively low frequency ($Q_{IP}:Q_{MP}:Q_{OP} = 4:30:200 \mu\text{L/h}$), (b) the effective droplet diameter of the outer droplet versus the applied voltage at low frequencies, (c) effect of the frequency which is within the low range, a constant voltage of $U=1.5$ kV is applied ($Q_{IP}:Q_{MP}:Q_{OP} = 4:30:200 \mu\text{L/h}$), (d) quantitative measurement of the effective diameter of the outer droplet varying with the applied frequencies with the low range.

Scale bars represent $100 \mu\text{m}$.

Next, the configuration is changed for applying the AC electric field (Figure 3-3(d), configuration 2) so that the field's direction is normal to the flow direction (normal direction for short). The influence of the voltage is firstly investigated as shown Figure 3-7(a): when the frequency f_e is fixed at 34.30 Hz (a relatively low value), the number of the core can be adjusted from 5 cores ($U=0.5$ kV) to stable single core ($U=1.5$ kV). A similar conclusion can be drawn that the control approach under the normally applied electric field by changing the applied voltage U with a low frequency f_e is effective and precise. A distinctive phenomenon comparing with the tangentially applied electric field (Figure 3-7(a)) is that the double emulsion is deformed along the normal direction indicating a strong influence of the electric field induced Maxwell stress T_M . The quantitatively measurement on the effective outer droplet diameter D_{out} shown in Figure 3-7(b) indicates a monotonic decreasing correlation with a good linearity within the range of applied voltages. The D_{out} changes from the original 250 μm to the final 100 μm when the voltage U reaches 1.5 kV. When the voltage is fixed at $U=1.5$ kV, the electric field is still capable of reducing D_{out} by means of the frequency f_e as shown in Figure 3-7(c) where the initially 3-core double emulsion becomes the single core double emulsion. The plotted correlation in Figure 3-7(d) between the D_{out} and f_e also gives a declining trend, however, without following a linear manner. The most effective range lies between 5 to 20 Hz, beyond which the function of the electric field is limited.

Figure 3-8 Effect of normal AC electric field with high frequencies on the formation of the O/W/O double emulsions: (a) voltage tuned O/W/O double emulsion generations with a fixed frequency of $f_e=1$ kHz ($Q_{IP}:Q_{MP}:Q_{OP}=2:30:200$ $\mu\text{L/h}$), (b) effective diameter of the outer droplet versus the applied voltage when the frequency is set 1 kHz, (c) frequency influenced O/W/O double emulsion generation with a constant $U=1.25$ kV ($Q_{IP}:Q_{MP}:Q_{OP}=4:30:200$ $\mu\text{L/h}$), (d) effective diameter of the outer droplet versus the applied frequency within the high rang with the $U=1.25$ kV. The scale bars equal 100 μm .

The electric field should be stronger when the f_e is high from the design of the electric circuit because the circuit equivalents to a high pass circuit when f_e is high. When the f_e is fixed at 1 kHz, the electric field deforms the double emulsion along the normal direction. However, the electric field triggered merging becomes dominant resulting in the irregular shapes of the double emulsions, hence the incapability of stable control (Figure 3-8 (a)). Although the size of the outer droplet D_{out} still follows a decreasing trend (Figure 3-8 (b)), the large error bar when voltage U is high, which is

due to the strong electric field which causes the merging and the electro spraying. When the high frequency f_e is used with a constant voltage of $U=1.25$ kV, the merging and electric spraying is turning significant over an increasing frequency f_e as shown in Figure 3-8 (c). The formation pattern becomes highly unstable and surprisingly, an increasing trend of the D_{out} over the frequency f_e (Figure 3-8 (d)) is observed, which can be explained by the dominating merging.

3.4 AC electric field controlled merging of the core droplets in W/O/W double emulsions

One of the distinct advantages of the double emulsions in microfluidic platform is that it offers new approaches for chemical reactions and material synthesis with unprecedented resolution and high efficiency due to the enhanced surface to volume ratio at microscale. Recent proposed novel approaches ranging from the micro reactions to single-cell-resolution encapsulations [155, 156, 158] are built on the manipulations of the double emulsions in microfluidic platform. In this section, a different design is utilized (Figure 3-9) to manipulate the dynamic behavior of the W/O/W double emulsions. In particular, the merging of the inner cores is triggered by applying the AC electric field in the tangential direction for both the single core (one-step) and double core (two-steps) merging, respectively.

Figure 3-9 Experimental design for W/O/W double emulsion with distinct cores.

Merging of the two cores in the W/O/W double emulsions is observed as shown Figure 3-10(a). Starting with the two cores approaching each other (Figure 3-10(a)), the dipole-dipole interaction becomes stronger so that the electric field induced stress $\vec{F}_E \propto \varepsilon(V/d)^2$ [169] is enough to overcome the capillary pressure $\vec{F}_{sf} \propto \gamma/R$ leading to the deformation of the interface ($t=39$ ms and $t=102$ ms), where ε is the electric permittivity, V is the voltage of the electric field, d is the space between the two (groups of) electrodes that connect the high voltage and the ground respectively, γ represents the interfacial tension and R denotes the radius of the core. Then the merge happens at $t=103$ ms, followed by the redistribution of the samples within the two cores ($t=106$ ms) after which the two cores become one ($t=118$ ms). The situations of merging more than two cores inside the W/O/W emulsions are also investigated as shown in Figure 3-10(a), where double emulsions with three cores is generated in channel. Similarly, with the aforementioned scenario,

two of the cores merge initially via the electric field induced stress $\vec{F}_E$ ($t=0\sim 11$ ms). As the resultant core (the bigger core) approaches the third core, due to the dipole-dipole interaction which deforms the interface ($t=92$ ms), the merge occurs for the second time ($t=97$ ms) so that in the end the three cores become one single core.

Figure 3-10 AC electric field-triggered merging of the cores within W/O/W double emulsions. (a) Dynamic procedure of double-core merging (single step) triggered by the electric field, (b) dynamics of the triple-core merging (two steps) triggered by the electric field, (c) electric field-induced merging of two distinct core droplets, one of which is marked by a fluorescent dye while the other is not; the dynamics were captured under fluorescence microscopy. The applied AC electric fields were $U = 1.25$ kV, $f_e = 1$ kHz for (a and b), $U = 1.3$ kV and $f_e = 1$ kHz for (c). All the electric fields were applied in the tangential direction, where the high voltage was employed downstream. The flow rate conditions were $Q_{IP}:Q_{MP}:Q_{OP} = 5 : 35 : 300$ $\mu\text{L/h}$ and $7 : 35 : 250$ $\mu\text{L/h}$ for (a) and (b), respectively, while (c) was captured under the flow rate ratio of $Q_{IPA} : Q_{IPB} : Q_{MP} : Q_{OP} = 5 : 2 : 35 : 270$ $\mu\text{L/h}$. The scale bars equal 100 μm .

Previous work on merging of the cores has been reported [155], however, they require the double emulsions in the static state and the whole merging process for two inner droplets requires more than 10 s. Comparatively, our method improves on the efficiency of merging of the cores with constant flow rates (that they are in motion)

and the time scale of merging is reduced to the order of 100 ms which is amiable for “lab on a chip” applications. Both the single-step (two cores) and the two-step (three cores) merging are achieved in the microchannels, which provide great flexibility in practical applications of chemical reactions, catalysis and screening bioassays.

Results shown in Figure 3-10 (a) and (b) are controlled merging of two and three identical cores respectively while in practical applications merging of distinct cores holds greater values. To prove viability of our method, the W/O/W double emulsion with two distinct droplets using a modified “T plus flow focusing” configuration is generated, one of which is marked with fluorescent dye (Q_{IPA}) while the other is not (Q_{IPB}). The merging dynamics of the two cores is captured (Figure 3-10 (c)). After the merging happens ($t=0\sim3$ ms), to our surprise the core marked with the dye attempts to encapsulate the other core ($t=11$ ms and $t=22$ ms) after which the whole mixing is completed ($t=70$ ms and $t=83$ ms). Judging from the shape of the interface and the time scale for mixing, the electric stress $\vec{F}_E$ may take a leading factor. The detailed mixing dynamics is further investigated through the imaging processing procedure (Figure 3-11). The dye mixing efficiency during the coalescence is characterized by the change of the ratio of the dye area (A_f) and the coalescence droplets area (A) over time. At $t=10$ ms, the coalescence starts, a part of interfaces of the two inner droplets merge together, and at $t=105$ ms, A_f/A reaches 92%. The time needed for the coalescence is about 100ms, which is much faster than similar works reported [9, 16].

Figure 3-11 The coalescence process of two inner droplets and the change of the ratio of the dye area (A_f) and the coalescence droplets area (A) over the time; $Q_{IPA} : Q_{IPB} : Q_{MP} : Q_{OP} = 5:2:25:270 \mu\text{L/h}$; $U=1.3 \text{ kV}$, $f_e=1 \text{ kHz}$; (scale bar: $50 \mu\text{m}$).

3.5 Stability of double emulsion

The double emulsions generated under the electric field are collected outside of the microchannels to confirm the stability of their structures. The morphology of the double emulsion is influenced by the AC electric field (Figure 3-12 (a)). After flowing through the microchannels, the double emulsion recovers to sphere on the glass slide (Figure 3-12 (b)). The structure and the size of the double emulsions own high uniformity, indicating the great controllability and the stability of the technique.

Figure 3-12 The stability of the double emulsion formation. (a) Morphology of the emulsions under the electric field. (b) Emulsions (O/W/O) collected outside the microchannels. The scale bars represent 100 μm .

3.6 Discussion

3.6.1 Control the number of the cores in O/W/O emulsions

Figure 3-13 Controlling the number of cores in O/W/O emulsions through AC electric fields. (a) Tangentially applied AC electric field controlled the cores at a low frequency (Figure 3-3(c) configuration 1). (b) Normally applied AC electric field controlled the cores at a low frequency (Fig. 3-3 (d) configuration 2). (c) Voltage controlled cores with the tangential AC electric fields at a fixed frequency of $f_e = 1$ kHz (Fig. 3-3 (c) configuration 1). (d) Voltage controlled cores with the normally applied AC electric fields (Fig. 3-3 (d) configuration 2).

To pave the way to practical applications of the double emulsion, the controlling methodology is one of the keys. In this section, the validity of controlling the number of the cores by means of AC electric fields is reported. As shown in Figure 3-13, the AC electric field can execute a relative precise control over the number of the cores encapsulated in the O/W/O emulsions. Figure 3-13(a) and (b) demonstrate a novel control method by matching the frequency of the electric field (f_e) with the generation rate (f_c) of the cores. The electric field induced Maxwell stress T_M stimulates the interface between the middle and outer phases leading to a final breakup at a specified frequency which is in close relation with that of generation rate of the cores f_c . A frequency controlled strategy is unveiled that the number of the cores can be tuned from the original 5 to 1 by adjusting the ratio of the two frequencies f_c/f_e . A good control can be achieved as the ratio f_c/f_e is reaching one. By implementing the tangential fields, the number of the cores approximately equals the ratio f_c/f_e given $f_c/f_e \leq 2$, while it fails to follow the relation when $f_c/f_e = 7$ which is reasonable as it is larger than the original number of the cores 5. Similar situation occurs for the normally applied electric fields that the control strategy applies when $f_c/f_e \leq 3$ (Figure 3-13(b)). The frequency matching phenomena offers a readily control method for real applications, which to our best knowledge is reported for the first time.

With Figure 3-13 (a) and (b) focusing on the frequency induced control, the effect of the voltage is investigated in Figure 3-13 (c) and (d) at a fixed frequency $f_e=1$ kHz. Good controls via adjusting the voltage are shown in Figure 3-13(c) and (d) when the

AC electric fields are applied in the tangential and normal configurations respectively. The small error bar in Figure 3-13(c) indicates a steady and reliable control can be expected when the electric field is applied tangentially. It is worth noting that a threshold exists beyond which there will be no significant variations ($U=1$ kV for both Figure 3-13(c) and (d)).

Figure 3-14 Control mechanism of the AC electric field: controlling effects determined by the electric capillary number Ca_E . (a) The electric field was applied tangentially; (b) the electric field was applied normally.

Although the proposed voltage controlled method shown in Figure 3-13(c) and (d) gives great stability, the control mechanism is not as straight forward as the scenario in Figure 3-13 (a) and (b). To scale the relative importance of the two factors with the most significant effect which are Maxwell stress $\mathbf{T}_M$ and the interfacial tension γ , hence explain the controlling mechanism. The electric capillary number is employed here, defined as $Ca_E = \epsilon_{op} E^2 a / \gamma$ [11, 170, 171], where ϵ_{op} stands for the electric permittivity of the outer phase, a depicts the characteristic length, and γ is the interfacial tension between the middle phase and the outer phase. The electric field

strength E can be calculated as $E = (U/2\sqrt{2})/(2W_{ga} + W_{ch})$, where U is the peak to peak value of the applied voltage, W_{ga} and W_{ch} two geometrical parameters represent the distance between the electrodes and the fluid channels, the width of the fluid channels respectively. The characteristic length a is chosen as $100\text{ }\mu\text{m}$ and $300\text{ }\mu\text{m}$ for tangential and normally applied fields respectively. ε_{OP} and γ are measured to be $\varepsilon_{OP} = 2.8 \times 8.85 \times 10^{-12}\text{ F/m}$, $\gamma = 5.3\text{ mN/m}$ respectively (See details in Appendix A). As referred in both of the two electric configurations, the effective diameter decreases with an increasing electric capillary number Ca_E as a result of a strong Maxwell stress $\mathbf{T}_M$. Therefore, the number of cores encapsulated by the outer droplet is also reduced which explains the similarity of the two trends on the effective diameter and the number of the cores versus the Ca_E .

It is worth noting that when Ca_E exceeds the threshold around 1, the electric field plays little role on further reducing size of the outer droplet and there will be only one core left within the outer droplet. In both of the two electric field configurations (tangential and normal), stable formation of the double emulsion is achieved with $Ca_E < 1$, while on the contrary unstable formation occurs if $Ca_E > 1$ as implied by the subfigures in Figure 3-14 (a) and (b). Upon further increasing the Ca_E , instable formations of the double emulsion occur which is unamiable for practical control. Our results have shown that the electric capillary number Ca_E can be considered as a readily scaling for controlling of O/W/O double emulsions under electric fields.

3.7 Summary

In this chapter, the effectiveness of the AC electric field on manipulations of both O/W/O and W/O/W double emulsions is systematically investigated through the non-contact type of electrodes. For the O/W/O double emulsion, the electric fields are applied in both tangential and normal configurations (Figure 3-3 (c) and (d)). The results show that both configurations are capable of tuning the formation of the double emulsions and the number of the cores.

A novel tuning method is reported by matching the frequency of the core generation to that of the AC electric field. The electric capillary number Ca_E was adopted to analyze the effectiveness of the AC electric field applied at high frequencies, which offered a guideline for practical applications. For the W/O/W double emulsion, both one-step and two-step merging are achieved in the time scale of 100 milliseconds by utilizing the AC electric field which is by far the fastest merging ever reported in double emulsions. The manipulation technique of employing the AC electric field reported in this chapter has widened the application of the double emulsions in critical fields, such as material synthesis, drug delivery, bio-engineering, *etc.* And the techniques can be readily implemented in other complex droplet systems. Furthermore, the rich physics revealed here has shown the critical roles of the AC electric field on controlling the interface within double emulsions.

Chapter 4 Dynamics of Droplet Formation in Flow-focusing Microchannel under AC Electric Fields [172]

4.1 Introduction

The electric field is one of the popular active droplet control techniques with the unique advantages of wide applicability and fast response on controlling [10, 125, 173]. Direct current (DC) [173] and alternate current (AC) [10, 11, 125] electric fields are both capable of tuning the droplet formation in microchannels due to the electric stress introduced at the liquid interfaces. However, the geometrical observation of microdroplet formation is limited under normal microscope conditions. The morphological analysis of the formation is difficult due to the challenges incurred in measuring the 3D morphology in fast speed. While the corresponding numerical investigations which further reveal the electrodynamics behind this emerging technique are relatively insufficient. The effect from the DC electric field on the droplet formation has been investigated numerically [72, 73]. Whereas the droplet formation under the AC electric field in microchannel still needs relevant numerical research to uncover the dynamics of how the electric voltage and the electric frequency influence the droplet formation. Especially, the mechanism behind the transition from dripping to jetting under electric field with high frequency observed in experiments is to be revealed.

In this chapter, the dynamics of droplet formation under AC electric field is investigated experimentally and numerically. Four non-contact electrodes are embedded around a flow-focusing geometry to implement the active droplet formation. The electric voltage and the electric frequency are proven to be able to tune the size of the droplet. A three-dimensional numerical model based on Volume of Fluid (VOF) [174-176] method was developed according to the experiments. The agreements in the droplet size control and the transition of formation regimes with the increase of the electric voltage and the electric frequency between the numerical results and the experimental ones prove the excellent reliability of the numerical model. With the increase of the electric voltage, the fluctuation of the electric stress enhances the interface instability, resulting in a formation of smaller droplet. The unstable droplet formation occurs when Ca_E reaches and goes beyond 1. Meanwhile, the pressure difference between the disperse phase and the continuous phase is gradually controlled by the electric field, which leads to the higher breakup rate of the disperse phase. The transition of the dripping to the jetting of the droplet formation occurs when $Ca_E > 1$. The magnitude of the electric body force at the neck interface lifts significantly during this transition, which is believed to be the reason for the transition. This work seeks to reveal the electrodynamics of the droplet formation under the AC electric field. The effects of the electric voltage and the frequency are clarified.

4.2 Numerical and experimental setups

As shown in Figure 4-1, a symmetrical flow-focusing geometry is chosen to generate the water in oil droplet. Deionized water is used as the disperse phase, and mineral oil flows as the continuous phase. Four non-contact electrodes are set around the flow-focusing junction to apply the electric field. The upper two electrodes connect to the high voltage source and the two electrodes at the downstream connect to the ground. All fluid channel shares the same width (W_{ch}) of 100 μm and the height (H_{ch}) of 35 μm . The gap between the electrode and the fluid channel (W_{ga}) is 50 μm (Figure 4-1 (a) and (b)). Correspondingly, a three-dimensional geometry is considered in this work based on the microchannel used in experiments (Figure 4-1 (c) and (d)), including the PDMS domain and the fluid channel domain. With the software ANSYS Fluent, a volume of fluid (VOF) model is utilized for the simulation on two phase incompressible fluid flowing inside the fluid channel domain and a leaky dielectric model [177, 178] is adopted to study the electric field across the two domains.

Figure 4-1 Schematics of the flow-focusing microchannel with non-contact electrodes in the experiments and the numerical model: (a) set-up of the electric field around the fluid channel, (b) channel details, (c) numerical simulation domain and (d) the droplet formation under electric field in numerical simulation.

The governing equations for fluids flowing in the microchannel under the electric field can be expressed as:

$$\frac{\partial(\rho \vec{v})}{\partial t} + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla p + \nabla \cdot [\mu(\nabla \vec{v} + \nabla \vec{v}^T)] + \vec{F}_{sf} + \vec{F}_E \quad (4.1)$$

$$\nabla \cdot (\vec{v}) = 0 \quad (4.2)$$

Where ρ , $\vec{v}$ and p are the fluid density and velocity vector and pressure, respectively. μ represents dynamic viscosity. The interfacial tension and the electric stress are considered as body forces $\vec{F}_{sf}$, $\vec{F}_e$ here.

The VOF model is used to analyse the interfacial dynamics of the two immiscible fluid flow for the droplet formation problem. In this model, the volume fraction α is used to imply the portion of the fluid in a computational cell: $\alpha_q = 1$ and $\alpha_q = 0$ represent the cell is filled with q th phase and the cell does not contain the q th phase, respectively. $0 < \alpha_q < 1$ represents the cell is occupied by the interface. In the two-phase system, $\alpha_1 = \alpha_2 = 0.5$ is considered as the location of the interface.

Specifically, in our two-phase system, the interface is determined by solving separate transport equation for the volume fraction of the secondary phase (α_2):

$$\frac{\partial \alpha_2}{\partial t} + \nabla \cdot (\alpha_2 \vec{v}) = 0 \quad (4.3)$$

Where ρ is the density. In this work, the water is the primary phase, the oil is the secondary phase. The volume fraction of the primary phase (α_1) and the secondary phase (α_2) will be computed based on the following constraint:

$$\alpha_1 + \alpha_2 = 1 \quad (4.4)$$

Interfacial tension force is modelled by[179]:

$$\vec{F}_{sf} = \gamma \frac{\rho \kappa \vec{n}}{\frac{1}{2}(\rho_1 + \rho_2)} \quad (4.5)$$

ρ_1 and ρ_2 are densities of the water phase and the oil phase. $\vec{n}$ is the gradient of α_1 , and $\kappa = \nabla \cdot \frac{\vec{n}}{|\vec{n}|}$. γ is the interfacial tension coefficient.

The electric stress can be defined by Maxwell stress tensor $\mathbf{T}_M$:

$$\mathbf{T}_M = \varepsilon(\vec{E}\vec{E} - \frac{1}{2}\vec{E} \cdot \vec{E}\mathbf{I}) \quad (4.6)$$

Where ε is the electric permittivity, $\vec{E}$ represents the electric field, and $\mathbf{I}$ is the identity tensor.

Determine of the electric stress is based on leaky dielectric model. The governing equations includes:

$$\frac{\partial \rho_f}{\partial t} + \nabla \cdot (\rho_f \vec{v} + \sigma \vec{E}) = 0 \quad (4.7)$$

Where $\rho_f = \nabla \cdot (\varepsilon \vec{E})$. σ is electric conductivity. The redistribution of charges is considered to be instantaneous [180], thus the equation becomes:

$$\nabla \cdot (\sigma \nabla \phi) = 0 \quad (4.8)$$

Where ϕ is the electric potential. The electric field is irrotational:

$$\nabla \times \vec{E} = 0 \quad (4.9)$$

The electric body force is determined by the divergence of the Maxwell stress tensor:

$$\vec{F}_E = \nabla \cdot \mathbf{T}_M \quad (4.10)$$

The effective electric properties of PDMS, mineral oil and water are adopted according to the literatures [181-183] (Table 4-1).

For the two-phase flow system, the following equations apply:

$$\rho = \rho_1\alpha_1 + \rho_2\alpha_2 \quad (4.11)$$

$$\mu = \mu_1\alpha_1 + \mu_2\alpha_2 \quad (4.12)$$

$$\varepsilon = \varepsilon_1\alpha_1 + \varepsilon_2\alpha_2 \quad (4.13)$$

$$\sigma = \sigma_1\alpha_1 + \sigma_2\alpha_2 \quad (4.14)$$

The average velocities are set for the disperse phase inlet and the continuous phase inlets, which are calculated from the volume flow rates for the disperse phase (Q_d) and continuous phase (Q_c) used by experiments, respectively. The non-slip wall boundary condition is applied for channel wall, which is non-wetting by the disperse phase [61, 70]. The outer boundary of the PDMS domain is electric insulation, including the inlets and the outlet. The static pressure condition is applied for the fluid outlet of the fluid channel. Gravity force is neglected in this model. The electric potential boundary condition ($V = U \sin(2\pi ft)$, U refers to the magnitude of the voltage, f represents the electric frequency and t is the time) is applied at the outer surface of PDMS domains, corresponding to the upstream electrodes in experiments. The other two electrodes are grounded ($V = 0$ V). The effective conductivities of the materials presented in this work are set according to relevant literatures [184-187]. The relative permittivity of DI water and mineral oil is 78 and 2 respectively. The dynamic viscosity of the DI water and the mineral oil is 8.9×10^{-4} Pa·s and 3×10^{-2} Pa·s, respectively. According to the measurement conducted by the pendent drop method using the tensiometer (FTA 200), the interfacial tension between the two fluids is set to be 7 mN/m (Please see Appendix B for details of measurements).

The control volume finite-difference technique is used for solving the governing equations. The laminar model is adopted to simulate the flowing due to the small Reynolds number in microchannel ($Re < 8$). The momentum equations are discretized with the second order upwind scheme. The semi-implicit method for pressure linked equations algorithm is used for pressure-velocity coupling. The volume fraction equation in VOF is solved with the implicit scheme. The time step is automatically tuned according to the global Courant number to ensure it is smaller than 0.5, and certain limitation is utilized for capturing key time points (for example, the time point where the voltage reaches extreme values).

Hexahedron cell is used to compose the mesh for the whole geometry. A mesh sensitivity test is conducted to determine mesh resolution. The diameter of the droplet generated is investigated by increasing the number of elements in the mesh. Considering the balance between the computational cost and the reliability of the results, a mesh consists of 382000 elements is used in this study (Figure 4-2). Initially, the interface of the two phases is set near the inlet of disperse phase. The initial velocity and the initial electric potential in the computational domain are set zero.

Figure 4-2 The mesh used by the simulation. The red lines represent the channel wall and the locations of electrode boundary conditions.

The mesh at the channel junction area is refined for capturing the dynamics of the droplet formation. The length of the hexahedron used at the junction area is $2.8\ \mu\text{m}$.

A mesh independence study is conducted under the electric conditions ($U = 500\ \text{V}$, $f = 500\ \text{Hz}$). After the number of elements reaches 382000, the results obtained did not generate a noticeable difference ($< 3\%$) with the increase of mesh elements, thus a mesh consists of 382000 elements is used in this study (Figure 4-3).

Figure 4-3 Results from one mesh independence study, a mesh consists of 382000 elements is used in this study.

The experiments are conducted with the PDMS flow-focusing microchannel, which is fabricated with soft-lithography technique. The PDMS chip with the flowing focusing pattern is bonded to the glass slide with thin PDMS coating to form the channels. The oxygen plasma cleaner (Harrick Plasma) is used for the bonding process.

Four electrodes embed around the flow-focusing junction symmetrically. The disperse phase is pumped into the centre channel and the continuous phase is pumped into the two side channels. Fluids are pumped by the high-precision syringe pump system (Centoni neMESYS) controlled by the computer.

Two upper electrodes connect the high voltage amplifier and the lower two electrodes connect the ground. The AC electric signal is generated by a waveform generator and amplified by the voltage amplifier which owns a constant amplification factor of 1000.

The experimental images are observed under an inverted microscope (Leica DM ILM) and recorded by a high-speed camera (Phantom V611). The record system is controlled by the computer (Figure 4-4).

Figure 4-4 Experimental set-up for the droplet formation under AC electric field in microchannel.

4.3 Results and discussion

4.3.1 Validation of numerical model

To validate of the numerical model, four electric voltages (peak voltage) ($U=250$ V, 500 V, 750 V and 1000V) and five electric frequencies ($f_e= 500$ Hz, 1000 Hz, 2000 Hz, 5000Hz and 7000 Hz) are applied on three flow rate conditions ($Q_d:Q_c = 50:100, 50:200, 100:400 \mu\text{L/h}$). Under the application of electric field, the Maxwell stress is produced on the fluidic interfaces. Figure 4-5 shows the comparison between the experimental and the numerical results. Effective diameter ($D = 2\sqrt{A/\pi}$, A is the area enclosure by the droplet) is adopted to characterize the size of the droplet. Due to the AC electric induced intense oscillation at the W/O interfaces, especially at

the junction area, under fixed flow rates, smaller droplets are generated compared to the no electric field cases (Figure 4-5(a)). To scale the relative importance between the electric stress and the interfacial tension, the electric capillary number is employed here: $Ca_E = \varepsilon_c E^2 a / \gamma$ [11, 188, 189], where ε_c is the permittivity of the continuous phase, a and γ represent the characteristic length scale and the interfacial tension coefficient, respectively. E refers to the electric field strength, which is calculated using the equation: $E = (U_d / \sqrt{2}) / W_{ch}$. U_d is the electric potential at point d (Figure 4-1 (c)) in simulations when V reaches maximum value. Higher U and f_e lead to greater U_d in the simulations, thus Ca_E increases with the rise of U and f_e .

With the increase of electric voltages, Ca_E ranges from 0 to 1.18, the oscillation at the interfaces of the disperse phase neck becomes more intense, which leads to a higher generation rate of droplets (Figure 4-5 (a)). Under the case of $Q_d:Q_c = 100:400 \mu\text{L}/\text{h}$, when $Ca_E > 1$, the generations of the droplets in the simulation and the experiment turn to be unstable, the deviation of the droplet size becomes larger (Figure 4-5 (b)). Under $Q_d:Q_c = 50:200 \mu\text{L}/\text{h}$, the unstable formations also occur when $Ca_E > 1$.

With fixed voltage of 750 V, increasing electric frequency leads to growing Ca_E . until the frequency reaches 2000 Hz ($Ca_E = 0.932$), the droplet formation maintains in dripping stage, where the droplets produced at the junction area (Figure 4-5 (a)). However, further increasing the electric frequency to 5000 Hz ($Ca_E = 1.320$) leads to a transition of droplet formation regime from dripping to jetting without changing the

flow rates. Meanwhile, a rise of droplet size is observed (Figure 4-5(c)). The jetting exhibits a long neck of the disperse phase extends across the channel junction. The further increase of Ca_E to 1.644 makes this neck longer and the droplet size smaller. Notably, it reduces the deviation of the droplet size compared to that of the dripping regime.

The agreement of the interface morphology and the droplet size between the simulations and the experiments shown in Figure 4-5 proves that the numerical model possess excellent reliability in predicting the dynamics of droplet formation under the AC electric field.

Figure 4-5 The comparisons between the results from experiments and simulations. (a) Comparison between the morphologies of interfaces from the experiments and the simulations (Scale bar: 100 μm). (b) Effective diameters obtained from the experiments and simulations under three flow rate conditions with different voltages ($U=0, 250, 500, 750, 1000$ V, $f_e=500$ Hz). (c) Comparison between the experiments and the simulations of the droplet diameter with five electric frequencies ($f_e=500, 1000, 2000, 5000, 7000$ Hz, $U=750$ V, $Q_d:Q_c = 100:400$ $\mu\text{L/h}$).

4.3.2 *Effects of AC electric field on droplet formation*

After the electric field is activated, the potential gradient is generated across the PDMS domain and the fluid channel domain. Free and bound charges induced by the electric field accumulate at the liquid interfaces and thus the Maxwell stress affects the movement of the interfaces together with the interfacial tension stress, viscous stress, and inertia stress. Because of the transition of voltage on the electrodes, this electric effect on interfaces alternates accordingly as well. Figure 4-6 illustrates droplet formation process under the electric field ($U=500$ V, $f_e=500$ Hz) and the transition of the transient velocity, transient electric potential and transient pressure where the demonstration at two time points ($V = 0$ V and -500 V) are made respectively.

At $t = 3$ ms, no electric field is formed inside the domains due to the zero potential ($V=0$ V) applied, thus the electric body force is zero in the whole computational domain. The disperse phase is recoiling to the upstream. While the electric field is formed in the domains at $t= 3.5$ ms, the electric body force ($\vec{F}_E$) acting at the interfaces induced by the electric field changes the dynamics of the droplet formation. Due to the accumulation of the free charges, the electric body force ($\vec{F}_E$) concentrates at the tip of the disperse phase neck, tending to drag the disperse phase out of the upstream channel, thus increases the downward velocity of the disperse phase and decreases the pressure inside. The transition of the electric stress leads to the oscillation of the disperse phase neck and eventually, affects the droplet formation

together with the inertia and the viscous force, counteracting the interfacial tension and speeding up the breakup of the disperse phase and thus turning down the size of droplet under the fixed flow rate of the fluids.

Figure 4-6 The effects of the electric field on droplet formation ($U=500$ V, $f_e=500$ Hz). (a) The evolution of the morphology of disperse phase for droplet and the distributions of velocity in Y direction, velocity vectors, electric potential, pressure and electric body forces at two time points where V reaches (b) 0 V and (c) -500 V, respectively.

4.3.2.1 Effects of electric voltage

The increase of U results in bigger electric potential difference across the channel, thus greater electric stress at the liquid interfaces is generated. The growing Ca_E indicates that the electric stress gradually dominates the droplet formation. To reveal

the mechanism for smaller droplet generation, the pressure evolution during the droplet formation is investigated.

The oscillation on the liquid interfaces influences the pressure distribution in the fluid channel (Figure 4-6). The pressure at the point d (P_d) and point c (P_c) are collected from the numerical results (Figure 4-1(c)). These two points locate at the center of the cross-section of the fluid channels. Figure 4-7 demonstrates the evolutions of the pressure difference between the disperse phase and the continuous phase and the morphology of the disperse phase neck under different electric conditions. The start point is chosen at approximately $\frac{1}{2}T_{DG}$ before the breakup of disperse phase occurs, where T_{DG} is the period of one droplet generation. The breakup of disperse phase occurs at point e and g (Figure 4-7). In the absence of electric field (Figure 4-7(a)), after the last droplet breakup, the disperse phase recoils, which corresponds to the increase of $(P_d - P_c)$ (e₁ to f₁ in Figure 4-7(a)), and also explains why P_c is smaller than P_d . $(P_d - P_c)$ starts to decrease when the dispersed phase expands into the continuous phase till the next breakup occurs (f₁ to g₁ in Figure 4-7(a)) and thus the continuous phase is hindered while the dispersed phase is squeezed. As the disperse phase elongates along the downstream direction and is kept thinning, the pressure in the disperse phase grows and hence, $(P_d - P_c)$ increases until the next breakup occurs. In the whole process, $P_d - P_c$ exhibits a smooth evolution.

Figure 4-7 The evolutions of the disperse phase neck (between two breakups) and the pressure difference between the disperse phase and the continuous phase. (a) No electric field, (b) $U=500$ V, $f_e=500$ Hz, (c) $U=750$ V, $f_e=500$ Hz. The disperse phase breaks up at time points e and g . Dimensionless time $t^* = t/T_E$. T_E and T_{DG} is the period of the AC electric field and the droplet generation period, respectively. Real time t is given below the dimensionless time.

When $U = 500$ V, due to the impact of the electric stress on the fluids, $P_d - P_c$ is affected (Figure 4-7(b)). The periodic variation of the electric field strength results in fluctuation of $(P_d - P_c)$. Usually, a wave trough will form at the time when the electric voltage reaches the extremum ($t = \frac{n}{2}T_e$, n is non-negative integer, blue long dash line in Figure 4-7(b) and (c), period of electric field $T_e = \frac{1}{f_e}$), while when the electric voltage reaches zero $t = \frac{m}{4}T_e$ (m is positive odd integer, red short dash line in Figure 4-7(b)), a wave crest forms. However, the effect of the electric field is relatively limited, a similar evolution pattern of $(P_d - P_c)$ with that of no electric field case is still observed: after the droplet breakup, $(P_d - P_c)$ rises, declines and then rises again successively. But the fluctuation of pressure induced by the electric stress shortens both the rise and the decline process of $(P_d - P_c)$ in the Figure 4-7(a) and (b), in other words, which shortens the recoil process (e_2 to f_2 in Figure 4-7(b)) and the expand process (f_2 to g_2 in Figure 4-7(b)) after the breakup, speeding up the droplet formation ($T_{DG} \approx 3.25$ ms).

In the case of $U = 750$ V (Figure 4-7 (c)), the situation becomes distinctive from that of the case without no electric field because of the greater magnitude of the electric stress. At $t = \frac{n}{2}T_e$, the electric field drags the disperse phase to expand, while at $t = \frac{m}{4}T_e$, the interfacial tension stress pulls back the disperse phase. The evolution of $(P_d - P_c)$ is synchronized with the applied electric field, indicating an electric stress dominating scenario. After the droplet breakup, the recoil process almost disappears due to the drag effect of electric stress, and the expansion of the disperse phase is further

shortened by the electric field. This intense oscillation greatly enhances the capillary instability, resulting in a higher rate of droplet breakup ($T_{DG} \approx 1.875$ ms) and smaller droplet size.

4.3.2.2 Effects of electric frequency

Figure 4-8 The effects of increasing electric frequencies ($U=750$ V). (a) Electric potential distributions versus the frequencies, (b) the value of U_d determined by increasing frequencies and (c) distributions of electric body force along the disperse phase neck interfaces. The vector in (a) represents the direction of electric body force.

The magnitude of electric body force is normalized through $F_E^* = \overline{F_E} H_{ch} a / \gamma$. (All data are collected from the xy plane at centre of the channel when V reaches 750 V for the first time after one breakup of disperse phase)

The transition of the droplet formation regimes tuned by the AC electric field is successfully predicted in the simulation. With relatively low electric frequency ($f_e < 2000$ Hz), the electric field increases the generation rate of the droplets and reduces the droplet sizes. When the frequency is lifted to 5000 Hz, without changing of the flow rate condition, the formation regime transits from dripping to jetting, forming a long jet of the disperse phase across the junction (Figure 4-5(a)). With fixed flow rate conditions, the controlled transition shows that electric field plays a decisive role here.

With the same electric voltage, the electric potential distribution in the computational domain varies with the increase of the electric frequency due to the variation of the electric conductivities of mineral oil and PDMS material used to fabricate the chip (Table 4-1). Figure 4-8 (a) shows the distributions of electric potential, the interfaces of disperse phase neck and the direction of electric body force at the interfaces when V reaches 750 V ($U=750$ V) for the first time after one breakup of disperse phase. The electric body forces acting at the interfaces own the direction from the internal of disperse phase to the continuous phase. With the increase of electric frequency, the electric potential inside the disperse increases significantly (Figure 4-8(b)) and due to the relatively larger electric potential gradient at the interface of the disperse and continuous phases, the electric field strength at the interface become the strongest, resulting in greatest electric body force with the outward direction from the internal of the disperse phase. At the same time, the increasing Ca_E indicates the electric stress is

gradually dominating the formation, and after $Ca_E > 1$, the formation transits to jetting (Figure 4-5(c)).

Table 4-1 Electric conductivities of materials under different electric frequencies.

Electric frequency (Hz)	Conductivity of PDMS (S/m)	Conductivity of mineral oil (S/m)	Conductivity of DI water (S/m)
500	7.95E-11	2.47E-11	4.9E-5
1000	1.02E-10	2.48E-11	4.9E-5
2000	2.50E-10	2.48E-11	4.9E-5
5000	6.30E-10	2.49E-11	4.9E-5
7000	8.00E-10	2.49E-11	4.9E-5

The electric conductivities are obtained from the literatures[181-183]

To investigate the mechanism of this transition, the distribution of the electric body force is investigated. Figure 4-8(c) illustrates the evolution of the electric body force along the interfaces of disperse phase necks normalized by F_E^* ($F_E^* = \overline{F_E} H_{ch} a / \gamma$ where $\overline{F_E}$ is the average magnitude of the electric body force at the interface). F_E^* interprets the ratio between electric body force and interfacial tension force. In the cases of 500 Hz and 2000 Hz, the high-magnitude area of electric body force appears only at the original ($-10 \mu\text{m} < y < 20 \mu\text{m}$) and the tip ($120 \mu\text{m} < y < 150 \mu\text{m}$) segments of the interfaces of necks, while at the rest part of the necks, F_E^* is close to zero. However, in the cases of 5000 Hz and 7000 Hz, there are high-magnitude areas that emerge at the middle part of the neck ($60 \mu\text{m} < Y < 200 \mu\text{m}$), where the electric stress is strong enough to prevent necking of the disperse phase. Therefore, the disperse phase is capable to extend to the downstream, forming the jetting. Furthermore, the high-magnitude area of F_E in the case of $f_e = 5000$ Hz brings

the drag effects in x direction on the disperse phase, resulting in the increase of droplet size (Figure 4-5 (c)). When $f_e=7000$ Hz, due that the breakup location of disperse phase moves away from the high-magnitude area of F_E mentioned above, the drag effects of electric stress in x direction is weakened on the droplet formation, causing the decrease of droplet size.

4.4 Summary

Water in oil droplet formation in flow-focusing microfluidic device under AC electric field was investigated numerically and experimentally in this chapter. The results from the three-dimensional CFD simulation with the coupling of the VOF method and leaky dielectric model are in agreement with the corresponding experimental results. The simulation reproduces the process of the droplet formation under the AC electric field under increasing electric voltage and electric frequency.

The experimental and numerical results show that the droplet size becomes smaller with the increase in electric voltage, leading to growing impact from the electric field to the droplet formation. The method of Ca_E based on the numerical data is utilized to analyze the impact of electric field. When the electric voltage increases beyond a certain point $Ca_E>1$, the formation of the droplet becomes unstable, embodying the high deviation in the size distribution of the generated droplets. The pressure difference between the disperse phase and the continuous phase illustrates the details of the impact of the electric stress. The evolution of the pressure difference is

controlled by the periodically varying electric field when U reaches 750 V. Fluctuation of the pressure speeds up the disperse phase breakup. The results demonstrate the impact of the voltage of AC electric field on the droplet formation.

When Ca_E goes beyond 1, the droplet formation transits from dripping to jetting with the increase of electric frequency. The increase of the electric frequency results in a big lift of the electric potential within the disperse phase, thus inducing strong electric body force at the middle part of the disperse phase neck. Since the electric body force is directed from the inside to outside of the disperse phase, it becomes capable of preventing the disperse phase neck from breakup, resulting in the jetting formation of the droplet. The detailed investigation uncovers the mechanisms behind the transition of the droplet formation from dripping to jetting through increasing the frequency of applied AC electric field. The results also indicate the critical significance of Ca_E in droplet formation under AC electric field.

Chapter 5 Electric Scissors for Precise Generation of Organic Droplets in Microfluidics [190]

5.1 Introduction

Organic phase microdroplet has been widely utilized in various fields such as in microreactors [191-194], microcarrier [14, 17-19], bioscreening [20-22] and analytical chemistry [23-25]. All of them are built on the foundation of precise and high customizable manipulation of droplets. However, a universal controllable droplet generation approach for different organic phases is still a challenge due to the complicated hydrodynamic features and the wettability issue, which limit the application scope and controllability of existed droplet generation devices.

Microfluidic devices are usually served as a generation tool for microdroplets[21, 22, 191-193, 195], attributed to its high throughput of monodisperse droplets, single droplet level control ability [1] and especially, the accessibility for integration of external fields, which enables the active droplet generation by adding an extra dimension in droplet manipulation [42, 50]. Electric field (E-field) is widely adopted as an external field for tuning the water droplet formation [10, 11, 57, 173, 196, 197] and triggering the coalescence of droplets [9, 58] in microchannels owing to its unique advantage of fast response. The DC [9, 57, 173] and the AC [10, 11, 58] electric fields are proven to be capable of controlling the droplet formation and coalescence due to the electric field induces Maxwell stress at the liquid interfaces.

However, organic droplet formation in microchannels, at present, did not share the benefits brought by the electric field techniques. The controllability of O/W droplet formation still owns a large space for improvement. Besides, the surface treatment is an issue that cannot be avoided in O/W droplet formation due to the prevailing of Poly(dimethylsiloxane) (PDMS) in microfluidics device fabrication, which brings in difficulties for the formation of O/W droplets due to its hydrophobic surface property [198]. Even though different surface treatment methods for turning the PDMS surface into hydrophilic are proposed [119, 199-202], the extra work load and the influence of the wall smoothness hinder the development of O/W droplet formation in microfluidics devices [50, 203, 204].

According to the Chapter 3, the Maxwell stress generated at the liquid interfaces possess the direction from the aqueous phase to the oil phase. Inspired from it, in this chapter, taking advantage of the Maxwell stress induced by the electric field, an active formation technique of O/W droplet in a native PDMS microchannel without the surface treatment is demonstrated. This method uses DC and sinusoidal waveform AC electric field to trigger the breakup of the otherwise non-breakup layered flow of the organic phase, forming O/W droplets with controlled size. The voltage which alternates in the DC and the square waveform is able to “cut” the layered organic phase flow into disperse phase effectively, thus the breakup of the oil phase and the voltage alternation are fully synchronic. Our results show that the square wave electric field controlled droplet formation possesses an inverse linear relationship

between the electric frequency and the droplet size. Sinusoidal AC electric field is found to be able to trigger single breakup or continuous breakups of oil phase enabling the controlled droplet formation. Critical voltages for the triggered breakup under DC and AC electric fields are located and the systematic investigation on the square and the sinusoidal wave form electric field tuned O/W droplet formation is conducted. In the end, the utility of this approach on four widely used organic phases being the disperse phase is demonstrated. The same triggering and tuning function of the electric field on them is realized. The results prove that the technique allows the omitting of the surface treatment for O/W droplet formation in native PDMS microchannel and offers straightforward and precise controllability on droplet formation, which should benefit a wide range of applications in connection with organic droplets.

5.2 Materials and methods

Poly(dimethylsiloxane) (PDMS, viscosity 100 cSt), Mineral oil, 1-Octadecene (ODE), 1,6-Hexanediol diacrylate (HDDA) are used as the disperse phase. Deionized water (DI water) (Milli-Q grade II) with 70% Glycerol and 0.2% Tween 20 is used as the continuous phase. These chemicals are purchased from Sigma Aldrich and used without further purification.

Figure 5-1 Schematics of the microchannel and the configurations for applying electric fields. (a) Illustration of the microchannel, (b) enlarged view at the channel junction where the two electrodes are imbedded and the stable multi-layer flow is formed, and the different behaviors of the disperse phase under the voltage alternation as well as the sinusoidal waveform electric field.

A flow-focusing geometry is adopted to form the multi-layer flow. Three inlets for pumping the disperse phase and continuous phase into the channel are fabricated. Two non-contact type electrodes are imbedded after the flow-focusing junction (Figure 5-1).

The flow focusing microchannels are fabricated by the lithographic method with the poly(dimethylsiloxane) (PDMS, Dow Corning Sylgard 184 kit) curing and oxygen

plasma bonding process (Harrick Plasma, PDC-32G). The geometrical information is shown in Figure 5-2 and Table 5-1.

Figure 5-2 Geometry of the microchannel

Table 5-1 Geometry parameters

Parameters	Value (μm)
W_{ch}	100
W_{ga}	50
W_{ga2}	55
R_e	50

The microchannel is a symmetric geometry and the channels for electrodes share the same height of $60\ \mu\text{m}$ with the fluidic channels. The width of the electrodes is $100\ \mu\text{m}$.

The Centoni neMESYS high precision, pulse free syringe pump system and the gastight microliter syringes (Hamilton gastight) are used to pump the fluids into the

microchannels with the accuracy of microliter per hour. The flow phenomena are observed by a microscope (Leica DM ILM) and recorded through a high-speed camera (Phantom V611). The syringe pump and the camera are controlled by the software operating on the computer.

Electrodes are fabricated by melting indium alloy into the predesigned channels for electrode. Then the alloy is connected to the high voltage supply system or the ground via the electric wires. The voltage signal (V) is generated by the signal generator (Agilent 33500B waveform generator) and then amplified by a high voltage amplifier (Trek 5/80 high voltage amplifier).

Upon application of the high voltage to the electrode, electric field is generated across the area in between the pair of the electrodes where the fluidic sample is constrained by the channel. Induced free and bound charges accumulate at the liquid interfaces and thus the interaction between the charges and the electric field drives the interface to be perturbed. The interaction results from the Maxwell stress can be defined as:

$$\mathbf{T}_M = \varepsilon(\vec{E}\vec{E} - \frac{1}{2}\vec{E} \cdot \vec{E}\mathbf{I}) \quad (5.1)$$

Where ε is the electric permittivity, $\vec{E}$ represents the electric field, and $\mathbf{I}$ is the identity tensor. For flow fields of dielectric fluids under electric field, the dielectric force will be the main body of the electric force due to the low conductivity of fluid, which is activated when there is a gradient of permittivity across the fluid interfaces,

and it is in the direction from the fluid of higher permittivity to the fluid with lower permittivity [205, 206].

A “capacitance” model is utilized to describe the effects of the electric field on the “cutting” phenomena (Figure 5-3). Between two electrodes, there are PDMS layer, disperse phase and continuous phase within the electric field. Figure 5-3 (b) shows a simplified electric circuit model of the electric microchannel system, which consists of the capacitance of the PDMS layer C_{PDMS} and the fluid resistances R_C and capacitance of disperse phase C_D . The subscripts “C” and “D” represent the continuous phase and the disperse phase, respectively.

Figure 5-3 Effective capacitance model of the microchannel. (a) The channel setup and (b) the equivalent electric circuit.

5.3 Results and discussions

Poly(dimethylsiloxane) (PDMS) oil liquid is used firstly as the disperse phase to form the typical disperse-continuous flow through a flow-focusing junction. It's worth noting that the surface treatment for the PDMS based microchannels is omitted here which is necessary for conventional approach. Owing to the hydrophobic feature of PDMS based microchannel (water contact angle $\sim 100^\circ$) [198], the PDMS oil and the water flow as a stable multi-layer flow (Figure 5-1). The PDMS layer in the middle exhibits a stable width (W) in steady state without breakup. Two interfaces formed in the water-oil-water cladding system remains stable from the junction to the outlet. With fixed flow rate of continuous phase (Q_c), W can be readily tuned by changing the flow rate of disperse phase (Q_d). The properties of the fluids can be seen in Appendix B.

To investigate the influences of the electric field (E-field) on this flowing system, a systematic exploration with the DC, the square and the sinusoidal waveform E-fields is conducted.

5.3.1 DC and Square wave electric field controlled breakup of the disperse phase

In this section, the phenomenon under the impact of the DC and the square wave E-field is investigated. The voltage signal (V) is applied on one electrode. The results show that a perturbation toward the PDMS layer will be induced at the two interfaces

by the E-field the moments the DC E-field turns on or off. Higher voltage amplitude of the DC E-field leads to larger amplitude of this perturbation. When this perturbation is strong enough to overcome the hydrodynamic stress at the interfaces, the two interfaces will contact each other and merge at a certain position, thus “cut” the disperse phase here (see Figure 5-1 (b)). Then the disperse phase flows from upstream will restore to layered flowing again even the electric field still existed since the electric stress has been counteracted by hydrodynamic stress arising from the flow field [173, 206, 207].

To achieve the merge, the voltage of E-field is required to beyond a critical voltage (U_{cd}). Once the voltage is greater than the critical voltage, the disperse phase in steady state will be cut by continuous phase when the E-field is triggered on and off. With the increase of the width of PDMS phase, U_{cd} for cutting increases as well. Under 5 flow rate conditions ($Q_d:Q_c = 10:200, 15:200, 20:200, 25:200, 30:200 \mu\text{L} \cdot \text{h}^{-1}$), the width W increases from about $3.75 \mu\text{m}$ to $14.34 \mu\text{m}$, and the corresponding critical voltage (U_{cd}) varies from about 250 V to 1030 V (Figure 5-4 (b)).

Obviously, consecutive breakups of the disperse phase are necessary for successful droplet formation. Proceeding from the multilayer flow, the above discoveries indicate that the intervals between the breakups of disperse phase can completely be controlled by triggering of the electric field, thus, theoretically, every droplet can be tuned into on-demand size. This thought inspires us to exploit square waveform

E-field to form monodispersed droplets in the microchannels. A square waveform is chosen with the minimum voltage of 0 V and the duty cycle of 50% for the investigation. 500 V and 900 V are applied as the maximum voltage. The frequency of the E-field (f_e) changes from 0.25 Hz to 2 Hz. Under three flow rate conditions ($Q_d:Q_c = 10:200, 15:200, 20:200 \mu\text{L h}^{-1}$), The monodispersed O/W droplets is successfully generated in the hydrophobic microchannel without surface treatment. The E-field triggered consecutive breakup of PDMS oil phase (Figure 5-4 (a)), and the frequencies of the breakup are controlled by the E-field (Figure 5-4 (c)).

In $Q_d:Q_c = 15:200, 20:200 \mu\text{L} \cdot \text{h}^{-1}$ cases (Figure 5-4 (a)), with $f_e = 1.5$ Hz, the voltage step leads to the breakup of PDMS layer at $t=0$ ms, next the disperse phase at upstream recoils due to the interfacial tension and hydrodynamic stress arising from upstream, then drives the oil phase to penetrate the aqueous phase. Finally, the stable layered flow forms again ($t=329$ ms) followed by the second breakup which occurs at $t=334$ ms. In the time that follows, the interval between two contiguous breakups remains constant at 334 ms, which is approximately equal to half of the period of square wave ($\frac{1}{2}T_e$). The voltage step of E-field successfully triggers the breakup of PDMS layer every time it occurs.

Therefore, with the f_e varying from 0.25 Hz to 2 Hz, the interval time between breakups of PDMS layer fixes at $\frac{1}{2}T_e$, thus the breakup frequencies (f_b) follow $f_b = 2f_e$. Owing to the fixed volume flow rate of PDMS layer, the size of the droplets

generated can be controlled precisely by the E-field. Figure 5-4 (d) shows the effective diameters ($D = 2\sqrt{A/\pi}$, A is the area of the disperse phase enclosed by the interface) of droplets formed under the two flow rate conditions, which represents two linear relationships between the diameter and the frequency of E-field due to the synchronization effect as shown in Figure 5-4 (c). Due to the higher volume flow rate of PDMS, droplets formed under $Q_d:Q_c=20:200 \mu\text{L}\cdot\text{h}^{-1}$ own greater diameters. Besides, the slope of the fitting line of $Q_d:Q_c=20:200 \mu\text{L}\cdot\text{h}^{-1}$ case ($\approx -66.0 \mu\text{m}/\text{Hz}$) is also bigger than that of $Q_d:Q_c=15:200 \mu\text{L}\cdot\text{h}^{-1}$ case ($\approx -53.7 \mu\text{m}/\text{Hz}$). The linear relationship offers us a clear regulation for quantitative controlling of droplet formation.

However, this straightforward linear correlation cannot be maintained under the flow rate ratio of $Q_d:Q_c = 10:200 \mu\text{L h}^{-1}$. When the f_e reaches and beyond 1.5 Hz, f_b shifts to the same value as f_e rather than the aforementioned $2f_e$. As shown in Figure 5-4 (a), after a breakup, the PDMS stream recoils to the upstream. Because of the low flow rate, PDMS flow requires longer time to form the stable layered flow. At $t=334$ ms, the PDMS stream hasn't recovered back completely resulting in a relatively high width, therefore the second voltage transition of E-field at $t=334$ ms can only induced a perturbation without actually cutting the PDMS layer. However, the next voltage transition will be able to break up the PDMS layer successfully since the width of PDMS layer has recovered back to the initial stage. In that sense, every two voltage

transitions cut the PDMS layer which results in $f_b = f_e$. Considering this behaviour, there may exist a limitation on generation rate of droplet with the square wave E-field.

Figure 5-4 The cutting effect of voltage jump in the DC and the square waveform electric field. (a) The breakup of disperse in $\frac{1}{2}T_e$ under three flow rate conditions (scale bar: $100\text{ }\mu\text{m}$), $f_e = 1.5\text{ Hz}$, and the black area is the tip of electrode. (b) The critical voltage U_{cd} for the disperse phase breakup with the voltage transition when the DC electric field is activated. (c) The relationship between the breakup frequencies f_b and the square electric field frequencies f_e under three flow rate conditions. (d) The effective diameter D of droplets under different square electric field frequencies. The dash lines are linear fit lines.

5.3.2 AC electric field controlled breakup of disperse phase

AC E-field is widely adopted for tuning the generation of aqueous droplets in microfluidics devices due to its ability to promote the instability of liquid interfaces. In this section, the sinusoidal waveform voltage is applied ($V = U \sin(2\pi f_e t)$) across the channel to explore the influence of AC E-field on the flows. The flow rate of the disperse phase, electric peak-to-peak voltage (U), and electric frequency (f_e) are discussed.

Similar to DC E-field, the results indicate the AC E-field is also able to cut the PDMS layer. The oscillations of interfaces triggered by the AC E-field results in the coalescence of the continuous phase. This oscillation amplitude, similarly, is enhanced by increasing of the electric voltage at a given frequency. When the amplitude of oscillation is great enough, the coalescence of continuous phase across the disperse phase is achieved. And with a fixed electric frequency, two critical voltages can be defined (U_{c1} and U_{c2}) to distinguish three stages of the phenomenon in experiments, which are non-breakup, transition, continuous breakup respectively. The non-breakup stage: when the voltage is smaller than the critical voltage 1 (U_{c1}), the E-field fails to “cut” the PDMS layer, with the W/O interfaces being perturbed. The transition stage: when the voltage reaches the U_{c1} , the cutting occurs after the activation of E-field, but only for limited times, then the interfaces sustain oscillation without coalescence. The continuous breakup stage: when the voltage reaches and

exceeds the critical voltage 2 (U_{c2}), the breakup can occur continually and thus generate the monodispersed droplet consistently.

The voltage is gradually increased to locate the critical voltages (each time, the voltage is increased by 10 V). The partition of these three stages is shown in Figure 5-5 (a) at $f_e = 100$ Hz. The results indicate that when the width of PDMS layer is greater, a higher voltage is needed for the breakup of the PDMS layer, and the transition gap lies between the U_{c1} and U_{c2} is wider.

With different E-field frequencies, U_{c1} and U_{c2} differ (Figure 5-5 (b)). With $W \approx 10.98$ μm , when frequency ranges from 25 Hz to 100 Hz, both the U_{c1} and the U_{c2} drop sharply, and then they tend to be stable with higher frequencies up to 1000 Hz. The transition area keeps growing until f_e reaches 200 Hz.

The existence of U_{c1} and U_{c2} implies that the breakup of the PDMS layer can triggered for once or multiple times selectively.

After the continuous formation of droplets is achieved, in order to explore the controlling ability of AC E-field, a systematic investigation of the influences of the voltage U and the frequency f_e of E-field on the droplet generation is conducted. Our high-speed video records show that greater f_e and U result in stronger interfacial instability and thereby increase the breakup frequency of PDMS layer, generating smaller droplets.

Figure 5-5 The AC controlled breakup of disperse phase. (a) The partition of three stages of the breakup of disperse phase under five jet width conditions, (b) the partition of three stages of the breakup of disperse phase under different electric frequencies, $W \approx 9.87 \mu\text{m}$. (c) The droplet formed under different electric frequency (scale bar: $100 \mu\text{m}$). (d) Droplet effective diameters versus electric frequencies (scale bar: $100 \mu\text{m}$), $U = 3 \text{ kV}$ (e) The droplets formed under different electric voltages (scale bar: $100 \mu\text{m}$). (f) Droplet effective diameters versus electric voltages, $f_e = 100 \text{ Hz}$.

The dynamics of droplet formation under applied voltage and frequency are depicted in Figure 5-5 (c-f). The droplet size decreases with the increment of the voltage and the frequency (Figure 5-5 (c) and (e)). The effective diameter D is utilized to

characterize the droplet size here. According to Figure 5-5 (d), when the voltage ($U=3$ kV) goes far beyond U_{c2} , the diameters of droplets drop dramatically with the frequency increasing from 10 Hz to 100 Hz. However, with further increase of the frequency, it remains stable even that the frequency reaches 1000 Hz. The rate of droplet diameter change can be up to approximately 205% under the flow condition of $Q_d:Q_c = 30:200 \mu\text{L h}^{-1}$ with the electric frequency ranging from 25 Hz to 1000 Hz. The voltage is capable of tuning the size of droplets as well. With the voltage limited to 3.5 kV, monotonically decreasing trends for five flow rate conditions are obtained and shown in Figure 5-5 (d). The above results indicate that both the increased frequency and voltage can promote the interfacial instability leading to the breakup of the disperse phase. Compared to the frequency control method, the voltage control shows a more gradual reduction of droplet size.

According to the results, higher voltage is required to generate stronger electric field strength inside the channel to “cut” the thicker disperse phase layer (Figure 5-5 (a)). Figure 5-5 (b) and (d) indicates that the electric stress at the water-organic interfaces is dependent to the electric frequency. Based on the capacitance model, the electric field strength can be evaluated at the water-organic interface by calculating the dimensionless potential across the fluid channel (U_{Fluids}/U).

The capacitance (C_{PDMS}, C_D), capacitive impedance (Z_{PDMS}, Z_D) and resistance of continuous phase (Z_c) can be estimated as:

$$Z_c = \frac{L}{\kappa A} \approx \frac{W_c}{\sigma_c H_{ch} b} \quad (4.1)$$

$$C_D \approx \frac{\varepsilon_0 \varepsilon_{r,D} b H_{ch}}{W_D} \quad (4.2)$$

$$C_{PDMS} = \frac{\varepsilon_0 \varepsilon_{r,PDMS} b H_{ch}}{W_{ga}} \quad (4.3)$$

$$Z_{PDMS} \approx \frac{-j}{2\pi f C_{PDMS}} \quad (4.4)$$

$$Z_D \approx \frac{-j}{2\pi f C_D} \quad (4.4)$$

where the κ denotes the electric conductivity of the fluids. W_c , W_D , H_{ch} , b , W_{ga} represent the width of the continuous phase, the width of the disperse phase, the height of the channel, the length of the electrode area, and the width of the PDMS solid gap, respectively. σ_c represents the conductivity of continuous phase. $\varepsilon_{r,D}$ and $\varepsilon_{r,PDMS}$ denote the relative permittivity of disperse phase and PDMS layer, respectively. j is the imaginary unit.

The dimensionless voltage experienced by the fluids U_{Fluids}/U can be estimated by:

$$\frac{U_{Fluids}}{U} = \frac{Z_D + 2Z_c}{Z_D + 2Z_c + 2Z_{PDMS}} \quad (4.5)$$

The values of the parameters are measured or determined by the literatures: $W_c = 8.9 \times 10^{-5}$ m, $W_D = 1.1 \times 10^{-5}$ m, $\sigma_c = 1 \times 10^{-8}$ S/m, $\sigma_D = 2 \times 10^{-11}$ S/m, $H_{ch} = 3.5 \times 10^{-5}$ m, $b = 1 \times 10^{-4}$ m, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, $\varepsilon_{r,PDMS} = \varepsilon_{r,D} = 3$, $W_{ga} = 5 \times 10^{-5}$ m.

As shown in Figure 5-6, after a sharp rise, the value of U_{Fluids}/U enters a stable stage at $f_e = 200$ Hz (Tending to 1). The sharp rise of U_{Fluids}/U results in stronger electric

field strength at the liquid interfaces and thus, decrease the voltage (U) required to achieve the “cutting” of the disperse phase. However, due to the insensitivity of the potential across the fluid channel to the electric frequency after f_e reaches 200 Hz, the critical voltages (Figure 5-5 (b)) enters the stable low-value stage even when the frequency is increasing.

Furthermore, the droplet size also reaches a stable stage after a decrease at $f_e = 200$ Hz. Due to the high voltage is applied ($U = 3$ kV), the recovery of the disperse thread after the breakup (Figure 5-4) is believed to be the limiting factor to the further droplet size decreasing.

Figure 5-6 Comparison between U_{Fluid}/U and U_{cl} .

The organic droplet is collected from the microchannel on a flat glass slide (Figure 5-7). The images demonstrate the good stability of the droplet generated and the size of the droplet is controlled by the electric field, which guaranteed the applicability of the technique in practical applications.

Figure 5-7 Collected droplet generated under different electric field conditions. (Sinusoidal waveform AC electric field). The scale bar is 50 μm .

5.4 Approach applicability

The above droplet generation controlling strategy arise from the electric force toward the disperse phase, specifically for the previous case, PDMS oil, due to the permittivity difference at the interfaces, thus it is possible to observe the same phenomenon with other substances being the disperse phase, despite the different hydrodynamic characteristics. In order to investigate the applicability of this strategy, the PDMS oil is replaced with three other typical oil fluids (Mineral oil, HDDA, ODE) with different hydrodynamic properties (Appendix B), which are widely adopted in chemical and biological researches [19, 143, 208-213].

Specifically, PDMS oil is a widely used silicon-based organic polymer due to its versatility. It presents in cosmetic, food, lubricants and heat-resistant cover. HDDA is a monomer used in the manufacture of polymers, particularly useful for use in ultraviolet light cure applications. Mineral oil is widely used in cell culture,

mechanical and industrial fields, which is transparent and non-conductive. ODE is usually used as inexpensive organic solvent in material synthesis.

The experiments are conducted in the same microchannel and the continuous phase remains the same aqueous solution (70 wt% Glycerol, 0.2 wt% Tween 20 in DI water). Firstly, Square wave E-field is applied on the electrode 2 (Figure 5-1). The minimum and the maximum voltage are 0 V and 500 V, respectively. The period of square wave (T_e) varies from 4 s to 0.5 s. Next the Sinusoidal AC E-fields with a wide range of voltage (1 kV to 3.5 kV) and frequency (10 Hz to 1 kHz) are applied on the electrode 2 to investigate the influence of AC E-field on the flows.

The results (Figure 5-8) suggest that DC and Sinusoidal E-field are again able to “cut” the disperse phases with precise control for droplet formation. Under the square E-field, the transition of voltage on the electrode is still able to trigger the breakup of the disperse phase effectively (Figure 5-8 (a), (d)). The breakups of disperse phases occur immediately as the voltage alternate. Therefore, in all cases, interval times (Δt) between the breakups of disperse phase maintain the value equaling the half of the period of square E-field ($\Delta t = \frac{1}{2}T_e$).

In the cases with three disperse phases, the AC electric field induced the oscillation at the interfaces and thus triggered continuous breakup of the disperse phases. Due to the increase of breakup rate of the PDMS layer, the revolutions of effective diameter show that, with high voltages, the increases of U and f_e reduce the size of droplets

formed. Similar to that of the PDMS solution, the droplet sizes drop dramatically when electric frequency increases from 10 Hz to 100 Hz and then tend to be stable when the electric frequency increase further (Figure 5-8 (b) and (d)). While the increase of voltage reduces the droplet size with a relatively stable rate in experiments (Figure 5-8 (c) and (d)).

Figure 5-8 Electric field controlled droplet formation of HDDA, ODE and mineral oil. (a) Interval time between breakups versus the frequencies of square waveform electric field. (b) Variation of effective diameters under different frequencies of sinusoidal AC electric field. (c) Variation of effective diameters under different voltages of sinusoidal AC electric field. (d) The E-field cutting on three organic phases in microchannels.

Electric field still cut these three fluids into droplets with fine controllability regardless their great difference in hydrodynamic features, especially, the perfect synchronization between the electric frequency and the breakup frequency of disperse

phase is achieved among all three fluids. Our results indicate this potentially universal and reliable control approach for droplet formation is available on a broad range of organic solutions. This technique should benefit broad range of applications that require precise quantitatively control on the organic phase droplet and may raise new perspectives in the fields of micro-reaction, drug delivery, pharmaceuticals, food engineering.

5.5 Summary

In summary, a universal active control strategy capable of precisely controlling the breakup of oil phases for O/W droplet formations is demonstrated in this chapter. Unlike the conventional droplet formation system in microchannels, this approach adopts a stable multilayer flow as an initial state, utilizing the DC, square and sinusoidal E-fields to trigger the coalescence of the continuous phase and thus “cut” the disperse phase. The size of the resulting droplets can be tuned by adjusting the voltage and frequency of the electric field. This approach greatly reduces the requirements of the hydrodynamic properties and resolves the wettability issue of the materials for droplet formation and control.

Upon activation of the DC E-field the sharp transition of voltage is able to trigger the breakup of the disperse phase. The critical voltage is defined for the triggered breakup under different widths of the initial disperse phase. Hereby, in square wave E-field triggered droplet formations, the disperse phase breakups at every alternation of the

voltage. Therefore, the interval time between the breakups is controlled by varying the electric frequency, which results in a linear correlation with the electric frequency and the size of the droplet.

Under the sinusoidal wave E-field, the electric voltage and the frequency are discussed to explore the cutting behavior in three regimes, including, non-breakup, breakup, continuous breakup. Following which the dynamics of droplet formation under AC E-field in continuous breakup regime is addressed. The increase of the voltage and the frequency is found to increase the breakup rate of the disperse phase leading to a smaller droplet.

The E-field controlling approach is extended to three typical oil substances, Mineral oil, 1-Octadecene, and 1,6-Hexanediol diacrylate, which are widely used in chemical and biological applications. The precise control on the interval time between breakups of disperse phase with square wave E-field remains effective on these three fluids. The AC E-field controlled droplet formation was successfully conducted on these three fluids and proven that the voltage and frequency are capable to tune the size of the droplets. The results indicate this technique possesses brilliant applicability in controlling droplet formation of different oil-based solutions.

Chapter 6 One-step Preparation of Steerable Janus particles with Solidified Magnetic Compartment in Microchannels

6.1 Introduction

Janus droplets/particles are, in a broad sense, droplet/particle with two compartments of distinct features in such as shape, chemistry, electric or magnetic properties [214-216], leading to anisotropic characteristics. Commonly, Janus particle comes from solidifying the Janus droplet. Since the emergence of the Janus structure [217], numerous approaches for the generation have been developed and their applications have been extended into optics [218], biochemistry [219] and material synthesis [220]. For example, colloidosome [221, 222], sputtering [223, 224] and Langmuir-Blodgett method [225] have been adopted to fabricate Janus droplets or particles. However, these methods show difficulties in controlling the size and the configuration of the Janus structure [226, 227]. Recently, more studies utilize microfluidic devices to fabricate the Janus droplets due to their precise controllability on the microstructure formation [89, 94, 101, 103, 215, 216, 228, 229].

In recent years, since the magnetic interaction is generally not easily affected by the surface chemistry of particles and properties of the outer environment such as pH, ionic concentration, and temperature [229-233], the magnetic Janus particles have been proposed as steerable and active suspension for applications in drug delivery [27,

234], material synthesis [28], and micro-actuators [235]. However, controlling the structure of the two compartments of the Janus particles during the formation and improving the efficiency of the transportation of the Janus particles driven by the magnetic field remains challenging.

In this chapter, a microfluidic device combining UV light to fabricate the half-solidified Janus particle in a one-step manner is introduced. Nano Fe_3O_4 particles are isolated in a UV curable polymer compartment of the Janus droplet which turns into the solid form after the UV initiated solidification process while the other compartment is filled with liquid oil. This structure ensures the separation of the two compartments thus avoids contamination between them. Solidified magnetic compartment improves the efficiency of the magnetic interaction between the nano Fe_3O_4 particle and the magnetic field. The size and the ratio between the two compartments are well controlled by the hydrodynamic conditions in the microchannel. Magnetic-field-controlled rotation of the Janus particle is achieved by demonstrations of the fabricated Janus particles acting as micro stirrers. This half-solidified structure favorites the Janus particle with a highly efficient and steerable microcarrier for a liquid substance which can hardly be achieved by conventional magnetic Janus particles whose compartments are both in solid. Hence the proposed methodology greatly expands the application potential of the Janus particle.

6.2 Experimental setup

The basic experimental setup is composed of a microscope under white light configuration, a high camera and syringe pump systems. The experimental images are observed under an inverted microscope (Leica DM ILM) and recorded by a high-speed camera (Phantom V611). The record system is controlled by the computer. Fluids are pumped into the microchannels by the high-precision syringe pump system (Centoni neMESYS).

A flow-focusing junction is utilized to form the Janus droplet (Figure 6-1 (a) and (b)). Two disperse phase streams meet at the area just before the focusing junction. The PDMS microchannel is pre-coated with the polyvinyl alcohol (PVA) solution before the experiments to modify the channel wall to be hydrophilic [119]. The two disperse phases break up at the junction due the shear induced by the two continuous streams from the two sides. The Janus droplet with two distinct compartments is hence generated as shown in Figure 6-1 (c). The UV light shines the Janus droplet right after the formation downstream (Figure 6-1 (a)) when the UV initialized curing process starts simultaneously resulting in the solidification of the compartment with nano magnetic particles while the other compartment (the oil) is left intact. The required time for the solidification is approximately 0.2 s given the power density of the LED lamp is around 0.75 W/cm^2 with the emission peak at 365 nm. The width of the main channel W_{ch} is 100 μm and the height of the channel H_{ch} is 55 μm (Figure 6-2).

The high speed microparticle image velocimetry (μ PIV) investigation is conducted with a commercial μ PIV system (Dantech, 10 kHz double cavity pulse laser with phantom high speed camera V611). The water droplet with Janus particle inside is placed in an external magnetic field. 10 % (volume/volume percentage) orange fluorescent particles (Life Technology, 1 μ m, 540/560 nm) is dispersed in the aqueous phase for illumination purpose.

Figure 6-1 Schematics of the Janus droplet generated in the microchannels. (a) 3D illustration of the microchannel. (b) Janus droplets with magnetic compartment generating in the experiments. (c) Janus droplets collected off-chip.

Figure 6-2 The geometry of the microchannel

6.3 Materials

DI water with 10 wt% Poly (vinyl alcohol) (PVA) (viscosity: $1.5 \times 10^{-2} \text{ Pa} \cdot \text{s}$) is used as the continuous phase. Disperse phase A is mineral oil with 0.3 wt% span 80 and disperse phase B is (1,6-Hexanediol diacrylate) HDDA with 8 wt% 2-Hydroxy-2-methylpropiophenone being the photoinitiator and 10 wt% Fe_3O_4 nanoparticle (US Research Nanomaterials, size: 8 nm). The Fe_3O_4 nanoparticle is treated with the Oleylamine before adding into the HDDA to avoid aggregation of the nanoparticle in solvent. All the chemicals, unless listed separately, are purchased from Sigma Aldrich.

6.4 Results and discussions

6.4.1 Control of the morphology of the Janus droplet.

The two disperse phases break up at the same time and turn into the Janus droplet at the junction area, where the black dots are the Fe_3O_4 nanoparticles. In this section the

morphology of the Janus droplet is tuned by varying the flow rate conditions for the disperse phase A, B (Q_{dA} and Q_{dB}) and the continuous phase Q_c . The size of the Janus droplet and the area ratio between the two disperse phases were tuned in the experiments.

The effective diameter of the Janus droplet with different flow rate ratio between the continuous phase and the disperse phase was firstly studied. Four flow rates of the continuous phase ($Q_c = 150, 200, 250, 300 \mu\text{L/h}$) and five flow rate ratio ($Q_c/(Q_{dA}+Q_{dB}) = 2$ to 6) were investigated (Figure 6-3). Here, the flow rates of the two disperse phases were set to be equal ($Q_{dA} = Q_{dB}$).

Figure 6-3 The evolution of the Janus droplet generation in the microchannel under different flow rate conditions. (a) The effects of the flow rate ratio on the Janus droplet formation. (b) The change of the effective diameter D with different flow rate conditions.

The results (Figure 6-3 (a)) indicate that the greater ratio between the flow rates of continuous phase and the disperse phase leads to smaller Janus droplet size. Besides, even though the ratio keeps the same, with bigger flow rate of continuous phase (Q_c), the size of the droplet decreases (Figure 6-3 (b)). According to the results from Chapter 2 and related literature [11, 236], higher flow rate of the continuous phase

brings bigger Capillary number with greater viscous drag effect at the junction area resulting in the smaller droplet generated.

Figure 6-4 The tuning of the compartment ratio under different flow rate ratio between the two disperse phase.. The insert illustrates the area occupied by the magnetic nanoparticle (A_B). A denotes the area of the entire Janus droplet. The total flow rate of disperse phases ($Q_{dA}+Q_{dB}$) keeps constant ($80 \mu\text{L/h}$).

The ratio between the two compartments of the Janus droplet can be tuned by adjusting the flow rate ratio between the two disperse phases. The proportion of the ratio between the area occupied by the magnetic nanoparticle (A_M) and the whole Janus droplet area (A) inside the microchannel is investigated. Figure 6-4 shows the evolution of A_M/A with different flow rate ratio between the mineral oil (disperse phase A) and HDDA with magnetic nanoparticles (disperse phase B) (Q_{dA}/Q_{dB}). Three flow rates of continuous phase (Q_C) were investigated while the total flow rate of the disperse phases ($Q_{dA}+Q_{dB}$) were kept constant. When the flow rate ratio (Q_{dA}/Q_{dB})

increases, the area ratio (A_M/A) reduces in a linear manner, which shows the great controllability of this approach on the Janus particle structure

6.4.2 *Steering of the Janus particles*

After the formation of the Janus droplet at the flow-focusing junction, the Janus droplet will be exposed to the UV light for solidification process. Then, the Janus particles with the solidified compartment in the drops of continuous phase are generated in the microchannel. In the end, the Janus particles inside the continuous phase are collected on a glass slide.

Due to the magnetic nanoparticle inside the solidified compartment, the Janus particle can be steered efficiently via externally applied magnetic field. To illustrate the steerability, four electromagnets are placed symmetrically around the water drop with Janus particles inside (Figure 6-5), which is able to generate a rotary magnetic field at the center area of the device where the water drop is placed. The impact of the frequency of the applied rotary magnetic field (f_e) on the steering of the Janus droplet with different compartmental ratio is studied.

Figure 6-5 Schematic of the period magnetic field for steering the Janus droplets.

With the activated magnetic field, Janus particles with different ratios of the two compartments start to rotate rapidly (Figure 6-6 (a) and (b)). The satellite droplets (Black dots around the Janus droplet) in a large area near the Janus particle are triggered to move in circle, which demonstrates the stirring effect of the Janus particles. The localized vortex originating from the Janus particle in the fluid proves its ability to generate stirring at microscale which can hardly be accessed via conventional methods.

The controlled rotation of the Janus particle (Figure 6-6 (b)) also illustrates the ability of precisely controlling the orientation, which verifies the potential of the Janus particle being an steerable carrier for the substance inside the liquid compartment (mineral oil in this work). It is worth mentioning that the mineral oil part deforms during the rotation due to the centrifugal effect (Figure 6-6 (b)).

Figure 6-6 Rotation of the Janus droplets under the effects of magnetic field. (a) Composite image formed by video recorded for demonstration of the effects of rotation when the magnetic field is off and on (scale bar: 25 μm). (b) The rotation process of a Janus droplet ($f_e = 15$ Hz, scale bar: 25 μm).

To investigate the efficiency of the magnetic-field-controlled rotation, the angular velocities of Janus particles possessing similar sizes ($D \approx 84 \mu\text{m}$) but with different ratios of compartments are recorded under applied magnetic field whose frequency (f_m) ranges from 1 to 10 Hz. The results (Figure 6-7) indicate that the increase of f_m leads to the accelerating rotation of the Janus particles. Besides, larger ratios of magnetic compartment (more quantity of the magnetic nanoparticle) offer the Janus particle bigger torque under the same magnetic field, which brings in higher efficiency of the magnetic steering.

Figure 6-7 The angular velocity of the Janus droplets with different quantities of magnetic nanoparticles under the magnetic field with increasing frequency (f_m).

To further illustrate the magnetic-field-controlled rotation of the Janus particles, we characterized the flow field around the Janus particle with the microparticle image velocimetry (μ PIV) technique. A Janus particle with the diameter of 205 μm and $A_M/A=0.58$ is placed in the external magnetic field. Figure 6-8 shows the distributions of the velocity vectors and the vorticities obtained from the μ PIV measurement during the rotations. The clockwise flow around the particle is generated due to the rotation of the Janus particle with $f_m=1$ and 10 Hz, as shown in Figure 6-8 (a) and (b) respectively. Higher f_m results in greater magnitudes of the velocity and the vorticity in the fields, indicating a stronger vortex is formed. The vorticity (w_z) is calculated by $w_z = \frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y}$. Where the v_x and v_y denote the x and y component of the velocity,

respectively. The results quantitatively demonstrate the ability of vortex generation of the Janus particles.

Figure 6-8 The distribution of the velocity vectors and the vorticities. (a) $f_m=1$ Hz. (b) $f_m=10$ Hz. The length of the vector indicates the magnitude of the velocity and the maximum magnitude of the velocity in the fields is 0.00027 m/s.

6.5 Summary

In this chapter, a novel magnetic Janus particle as a steerable micro-scale suspension is generated through the microfluidic flow-focusing device, which consists of a liquid oil compartment and a solidified compartment containing magnetic nanoparticles. The controllability of the formation of the Janus droplet in the microfluidic device is studied firstly. And the controlling mechanism of both the size and the ratio between the two compartments of Janus droplets tuned by flow rate conditions is revealed. Secondly, the one-step fabrication process is achieved through the accurate UV curing of the magnetic compartment inside the microchannel. To verify the capability of the fabricated solidified Janus particles (only one of the two compartments is solidified), a custom-made rotary external magnetic field is applied for steering. Rapid rotation of

the Janus particle under the magnetic field is achieved and the relationship between the angular velocity of the Janus particles and the frequency of the applied magnetic field is revealed. Its ability of vortex generation is demonstrated through the μ PIV measurement, which proves the enormous potentials favored by the “half”-solidified steerable suspension in steerable material transport and micro-scale vortex generation, particularly in fields of chemical and biological applications.

Chapter 7 Conclusions and Future work

7.1 Conclusions

The emergence of microfluidics has gained intense research focus owing to its enormous potentials in scientific research and industrial production. Precise control of the formation of the microdroplets in microchannels has become the foundation of droplet-based applications. Furthermore, the active formation techniques, endowing another level of controllability in manipulating droplets at the microscale, have drawn increasing attention. The electric field, which is capable of inducing Maxwell stress at the liquid interface, has been proved to control the droplet generation in microfluidics efficiently. This thesis seeks to improve the controllability of the microdroplet formation in microchannels and explores its applications.

This thesis proposes active droplet formation strategies with the electric field for double emulsion for the first time and achieves ultra-fast electrocoalescence of droplets inside the double emulsions. To better understand the impact of the electric field on the droplet formation, the dynamics of the droplet formation in the flow-focusing microchannel under the AC electric field are explored by experiments and numerical simulations. For the first time, a universal electric field controlling approach for oil droplet formation is reported. Additionally, a novel half-solidified steerable Janus droplet is fabricated in the microchannels and utilized for active micro-scale vortex generation and substance transport.

The detailed conclusions are as follows:

- The hierarchical flow-focusing microchannels coupling with the electrodes were designed and fabricated for the investigation of the double emulsion droplet formation under the effects of an AC electric field. The dependency of the double emulsion sizes and the number of cores on the applied electric field were studied. The results show that both the electric voltage and frequency can precisely control the size of the double emulsion generated and the number of the cores inside. Furthermore, the ultra-fast coalescence of the cores inside the double emulsion triggered by the electric field was achieved in the microchannel. Controlled sequential coalescence between the cores was observed. This technique greatly improves the controllability of the double emulsion formation and benefits the double-emulsion-based applications.
- The water droplet formation in a flow-focusing microchannel under the AC electric field was experimentally and numerically investigated revealing the dynamic behind the electric-field-controlled droplet formation. The three-dimensional numerical model is combined with the VOF method and the leaky dielectric model to describe the flow field and the electric field inside the microchannel. The agreements between the numerical results and the experimental ones show the excellent reliability of the numerical model. To illustrate the effects of the electric field, the droplet size was analyzed through the

capillary number. The pressure differences of the flow field resulting from the electric field speeds up the breakup of the disperse phase, which leads to size reduction of the droplet. The study shows that the surge in the magnitude of the electric body force tends to stretch the disperse phase at liquid interfaces, which leads to the transition of the droplet formation regime from dripping to jetting. This numerical research reveals the dynamics behind AC electric-field-controlled droplet formation and thus provides a reliable reference for improvements of the droplet formation.

- Based on the features of the electric stress at the liquid interface, a flow-focusing microchannel coupling with electrodes was designed and fabricated to explore the organic droplet formation under the electric field. With the electric field, the organic droplet was successfully generated in a native PDMS microchannel without surface treatment. The size of the droplet was controlled precisely under the square wave and the sinusoid wave electric field. The electric voltage and the electric frequency can be used to tune the size of the droplet efficiently. To test the applicability, these control strategies were applied to four typical organic fluids, each flowing with different hydrodynamic characteristics. The results show the same precise cutting and tuning effects from the electric fields, which illustrates the brilliant applicability of the technique.

- A one-step generation strategy for the Janus particle with one solidified magnetic compartment was illustrated in the microchannel. The flow conditions of the fluids are able to tune the size of the Janus particle and the volume ratio between the two compartments. After the UV exposure, the solidified compartment with magnetic nanoparticles inside enables the particle to be a half-solidified steerable suspension in fluids. Utilizing a rotary external magnetic field, the controllable rotation of the Janus particle was observed. The dependency of the rotation angular speed on the frequency of the magnetic field was investigated. The results demonstrate the potential of the Janus particle for micro-scale vortex generation and steerable substance delivery.

7.2 Future works

Recently, the microfluidic device plays an increasingly important role in different fields, which requires more application-oriented research of microfluidic devices. A deeper and more comprehensive understanding of hydrodynamics in microfluidics thus becomes indispensable. On this basis, exploring its applications will be the next task. The future works of this thesis include further studies of the mechanism behind the experimental phenomena and introducing real application scenarios. The detailed future works are listed here:

- The dynamic of the double emulsion formation under the electric field can be further explored via experimental, numerical, and theoretical approaches. The

impact of the inner cores on the outer droplet formation should be investigated. Further systematic investigations on the influence of microchannel geometry and fluidic properties on the final controlling effect of the electric field on the formation of the double emulsion. Moreover, the study could be extended to fluids with complex rheological behavior due to their crucial roles in biological applications.

- The application of double emulsion should be explored. Double emulsions have great potentials in substance delivery, chemical reaction, and material synthesis. It is an ideal carrier of ingredients and a promising structure to accommodate the micro-reaction. As shown in the above experiments, the electric field offers precise control over the size and structure of the double emulsion as well as, the coalescence inside the double emulsion. Thus, double emulsions acting as the carrier with active ingredients or the reaction vessel for chemical testing can be explored.
- The numerical and theoretical studies should be expanded to Janus particles to improve the efficiencies of the formation and the magnetic controlling. The hydrodynamic of the formation process involving two disperse phases needs further investigations. The magnetohydrodynamic of the Janus particle steering should be further explored.

- The application of the magnetic Janus particle can be expanded. The steering strategy of the Janus particle should be further optimized for complex applications in the biological and chemical fields. The dynamics behind the interaction between the Janus particle and the magnetic field should be investigated. The potential for substance transport should be further verified and explored in real application scenarios.

Appendix A

Interfacial tension

Couple of fluids	Interfacial tension (mN/m)
DI water with 65 wt% Glycerol and Mineral oil with 5 wt% span 80	5.30±0.072

The interfacial tension is measured by the tensiometer, model: FTA 200, using pendent droplet method. The interfacial tension is measured for at least three times to ensure the repeatability.

Dielectric constant of the fluid

Fluid	Relative permittivity
Mineral oil with 5 wt% span 80	2.8

The dielectric constants of the fluid are measured by filling the fluid into a cylindrical shape. The capacitances with and without the fluids are measured by a precision LCR meter (Keysight E4980AL). The relative permittivity can then be calculated by the formula of $C = \varepsilon_0 \varepsilon_r A/d$.

O/W/O double emulsion formation under tangential AC electric field---other results

Figure 0-1 The change of the effective diameter of outer droplets with different outer phase's flow rates over the different (a) frequencies ($V_0=1$ KV) and (b) voltages ($f_e=1$ KHz).

Figure 0-2 The change of the effective diameter of outer droplets with different middle phase's flow rates over the different (a) frequencies ($V_0=1$ KV) and (b) voltages ($f_e=1$ KHz).

Figure 0-3 The change of the effective diameter of outer droplets with different inner phase's flow rates over the different (a) frequencies ($V_0=1 \text{ KV}$) and (b) voltages ($f_e=1 \text{ KHz}$).

Appendix B

Viscosity of the fluids

Table S-2 Viscosities of the fluids

Fluids	Viscosity (mPas)
70% w.t. Glycerol 0.2% w.t. in DI water	18
Poly(dimethylsiloxane), viscosity 100 cSt	97
Mineral oil	33
1-Octadecene	3
1,6-Hexanediol diacrylate	7
DI water	0.9

The viscosities are obtained by measuring with the TA instruments Discovery Hybrid Rheometer (DHR-2), the literature[237] and the supplier.

Interfacial tension between the fluids

Table S-3 Interfacial tension of the fluidic pairs

Fluidic pairs	Interfacial tension (mN/m)
70% w.t. Glycerol 0.2% w.t. Tween 20 in DI water/ Poly(dimethylsiloxane)	30.3
70% w.t. Glycerol 0.2% w.t. Tween 20 in DI water/ Mineral oil	3.8
70% w.t. Glycerol 0.2% w.t. Tween 20 in DI water/ 1-Octadecene	2.8
70% w.t. Glycerol 0.2% w.t. Tween 20 in DI water/ 1,6-Hexanediol diacrylate	56.7

The interfacial tensions are measured by the tensiometer (FTA 200), using pendent droplet method.

Dielectric constant of the fluids

Table S-4 Dielectric constant of the fluids

Fluids	Relative permittivity
70% w.t. Glycerol 0.2% w.t. in DI water	32.5

Poly(dimethylsiloxane)	1.9
Mineral oil	2
1-Octadecene	11.3
1,6-Hexanediol diacrylate	10.4
DI water	78

The dielectric constants are measure by filling the fluids into a capacitor. The capacitances are measured by a precision LCR meter (keysight E4980AL).

List of publications

- Huang, Y.¹, **Yin, S.**¹, Chong, W. H., Wong, T. N., & Ooi, K. T. (2019). Precise morphology control and fast merging of a complex multi-emulsion system: the effects of AC electric fields. *Soft matter*, 15(28), 5614-5625.
- **Yin, S.**, Huang, Y., Wong, T. N., & Ooi, K. T. (2020). Dynamics of Droplet Formation in Flow-focusing Microchannel under AC Electric Fields. *International Journal of Multiphase Flow*, 103212.
- **Yin, S.**, Huang, Y., Wong, T. N., Chong, W. H., & Ooi, K. T. (2019). Electric Scissors for Precise Generation of Organic Droplets in Microfluidics: A Universal Approach that Goes beyond Surface Wettability. *The Journal of Physical Chemistry C*, 123(42), 25643-25650.
- **Yin, S.**, Huang, Y., & Wong, T. N. (2021). Critical Conditions for Organic Thread Cutting under Electric Fields. *Soft Matter*.

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