

## Supplementary Information

### Electro-coalescence in Step Emulsification: Dynamics and Applications

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**ABSTRACT:** The supporting information includes the AC frequency-controlled coalescence, design of the device for droplet size control, fitting of the droplet sizes on flow rate and voltage and the simplification method for controlling equation of voltage. The supplementary videos include the production of tri-layered droplets and in-reservoir coalescence of flow tips.

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#### AC frequency-controlled coalescence

When AC electrical field is applied to the flow tips, the coalescence positions are also dependent on the frequency, as shown in Fig. S-1. The ratio  $d_c/d_0$  increases when the frequency increases in the range from 0 to 1.2kHz, above which the resident time is too long to trigger coalescence before the individual flow tips reach the edge of the terrace and start alternative dripping of two drop streams. The bound charges and the free charges have different responses to the AC frequency. Since the characteristic frequencies of the electronic, atomic and dipolar polarization of the bound charges at the interface are much higher (>MHz) than the AC frequency (<1.2kHz) used in this work, the polarization of the bound charges can be completed quickly as the electrical field inverses. However, the characteristic frequency of the ionic charge relaxation, which is determined by the salt concentration and the permittivity of dispersed and continuous phases, is much lower. The electro-migration of the free charges, i.e. the salt ions, is subject to obvious deceleration with the increase of AC frequency in the kHz order according to the results. At the same flow rate, increasing AC frequency means less free charges can be migrated to the interface during a half-cycle, which causes lower local electric field strength between the neighboring flow tips and thus longer resident time. Consequently, increasing AC frequency leads to larger  $d_c/d_0$ . Meanwhile, at different AC frequencies, the dependence of  $d_c/d_0$  on the flow rate is also different, which is a result of competition between the fluidic convection and the electro-migration. The electrical field migrate free charges to the interface while the convection of the dispersed fluidic remove them. The convection is mainly driven by the infusing of the dispersed fluid from the MCF channels and thus related to the flow rate. At low AC frequencies or DC voltage, the free charges are electro-migrated to the interface continuously and accumulating a large amount of free charges at the interface. The amount of the free charges removed by the convection is relatively small and thus the coalescence behavior is not sensitive to the flow rate. By contrast, at high AC frequencies, the electrical field inverses quickly. During a half-cycle, only a small amount of free charges is moved to interface. The accumulation of the free charges is more sensitive to the fluidic convection. As a result,  $d_c/d_0$  is larger at higher flow rate, which is noticeable at high AC frequency, as shown in Fig. S-1.

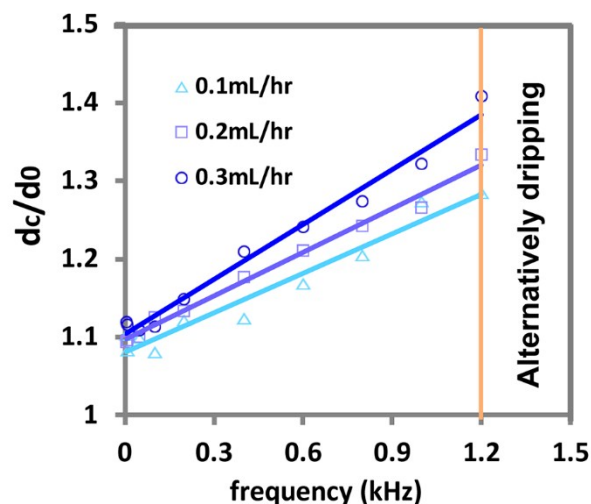
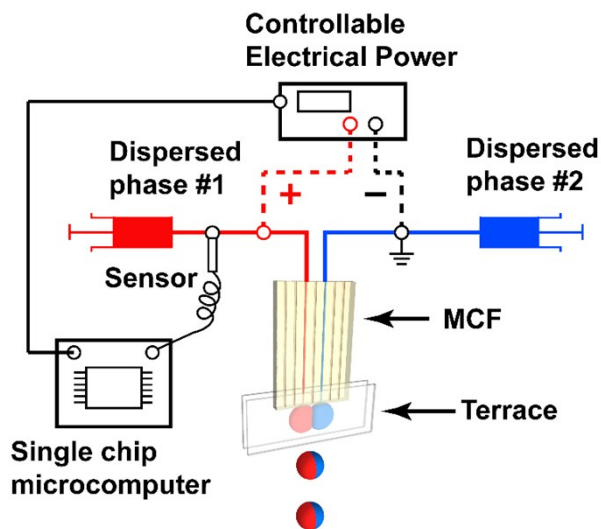


Figure S-1. the dependence of  $d_c/d_0$  on the AC frequency.

### Device for droplet size control

The device for droplet size control is modified from the typical device described in the manuscript (Figure 1(A)). Specifically, a flow rate sensor (Meacon Co. Ltd.) is mounted to the tube connecting the syringe and the MCF. Since the flow rate is equal in the droplet size control section, only one of the flow rates are detected. A single chip microcomputer (STM32) is used to read the flow rate and calculate the voltage according to controlling equations of voltage. Then, a controllable electrical power (Hanshengpuyuan Co. Ltd.), instead of a signal generator in the typical device, is used to output the DC voltage to the electrodes in the tubes. The codes are written in the computer and then copied to the single chip microcomputer by I/O module. The schematic picture of the device is shown in Fig S-2.

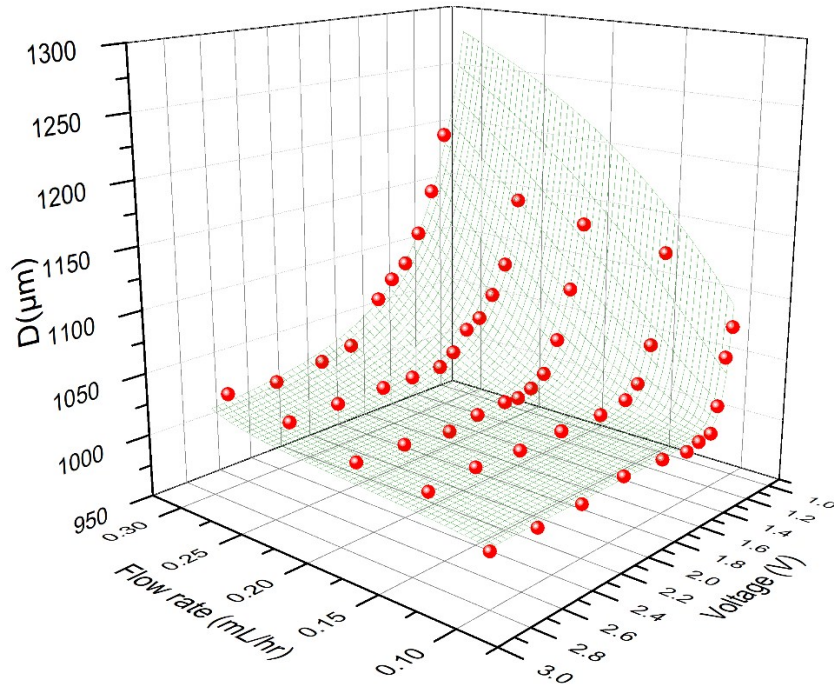


**Figure S-2** Device for droplet size control. A flow rate sensor and a single chip microcomputer are used to detect the flow rate and calculate the voltage accordingly. A controllable electrical power is used to communicate with the single chip microcomputer and output the DC voltage.

### Fitting of the droplet sizes on flow rate and voltage

To control the dependence of the drop sizes on the flow rate, we need an accurate model of the drop sizes instead of using the equation (10) in the manuscript. So the binary functional fitting for the drop sizes is conducted by Origin 8.5.

The fitting result is  $D = 319.91/V^{2.69/Q^{1.05} - 6.24} + 13977.53 \times Q^{9.94 \times 10^{-4}} - 12950.70$  with  $R^2=0.97$ . The meshed surface shows the fitting result while the red dots are the experimental results. The droplet sizes obtained at the flow rate of 0.15 and 0.25 mL/hr are also plotted in Fig. S-3 but not used in fitting, because too much raw data fail the fitting. Fig. S-3 shows that the extra data also agrees well with the fitting result.



**Figure S-3** Fitting of droplet sizes on flow rate and voltage

### Simplification of Controlling equations of voltage V1 and V2

The controlling equations of voltage can be obtained by combing the target dependence equations of droplet size on flow rate with the above fitting equation of droplet sizes. However, since the fitting equation is complex, the controlling equations of voltage are also complex, which is not good for fast calculation and output of the single chip microcomputer and causes error. Therefore, we actually use simple polynomial equations to replace the complex equations. Specifically, the controlling equation for droplet size of  $D=500Q+950$  is

$$V_1 = \left( \frac{319.91}{13900.70 + 500Q - 13977.53Q^{9.94 \times 10^{-4}}} \right)^{\frac{1}{2.69/Q^{1.05} - 6.24}}$$

We plot  $V$  vs  $Q$  and fit it with a quadratic function. The result is  $V_1=6.30Q^2-1.15Q+1.24$ , which we actually use. The value of  $R^2$  is 0.9986. Difference between the accurate equation and the quadratic equation is very minor, as shown the Fig. S-4.

Similarly, when the target droplet size is  $D=1050\mu\text{m}$ , the accurate controlling equation is

$$V_2 = \left( \frac{319.91}{14000.70 - 13977.53Q^{9.94 \times 10^{-4}}} \right)^{\frac{1}{2.69/Q^{1.05} - 6.24}}$$

It can be replaced by a cubic function as  $V_2=114.75Q^3-47.97Q^2+8.26Q+0.61$  while  $R^2=0.9993$  as shown in Fig. S-4. The highly accurate approximations ensure the precision of the output voltage.

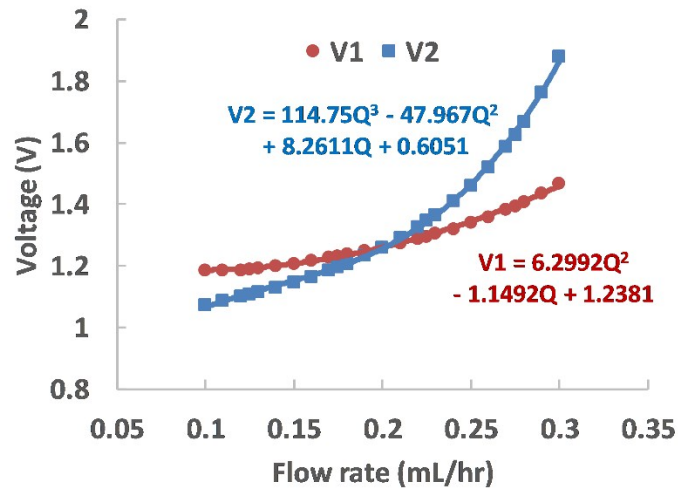


Figure S-4 Simplification of controlling equation of voltages. The dots show the accurate value of the controlling voltages while the solid lines show the approximating voltages actually used.

**Supplementary video 1:** in-reservoir coalescence of flow tips. The voltage keeps 5V.

**Supplementary video 2:** production of tri-layered droplets. The voltage keeps 10V constantly throughout the droplet production process. DI water with 1wt% sodium chloride is used as dispersed fluid here.