Supporting information

Ultra small droplet generation via volatile component evaporation

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Materials and equipments:

Fc40 was obtained from 3M company. Sylgard 184 PDMS oligomer and curing agent were from Dow Corning (Midland, MI). SU-8 (3035) photoresist was purchased from MicroChem. DMSO and tetrabutyl titanate was from Shanghai Ling Feng Chemical Reagent Co. Ltd. Ethanol was from Xilong Chemical Engneering Co.Ltd. Acetone was from Shanghai Chemical Reagent Co. Ltd. 1H,1H,2H,2H-perfluorooctyltrichlorosilane was from J&K Scientific Ltd. The surfactant used in oil is Krytox®FSL157 obtained from DuPont.

Syringe pumps (Longerpump, L0107-3A, Hebei, China) were used to deliver different phases to the microfluidic device. The observation of droplet was conducted on a platform of an epifluorescence microscope (Olympus IX71) equipped with an 10× or 40× objective and an Evolve 512 electron-multiplied charge-coupled device from Photometrics (EMCCD; Tucson, USA). Image J and Excel software were used to process data.

Fabrication and modification of microfluidic device

The PDMS microfluidic device was composed of PDMS and glass, and fabricated by standard soft lithography process. The layout of microdevice and detail parameters of flow focusing geometry are shown in figure S1a. All fabricated microchannel has the same height of 30um. After the bonding of PDMS and glass plate, 2% (v/v) 1H,1H,2H,2H-perfluorooctyltrichlorosilane solution resolved in Fc40 was pipetted into microchannel by a pipette gun. Then the microdevice was placed for 20min. After that, the solution in microchannel was removed by vacuum and washed by ethanol for several times.

The droplet generation in flow focusing microdevice

The dispersion phase and continuous phase were injected into microdevice by three syringe pump. Droplets were generated at the orifice uniformly and stably. Then, we observed droplet size in Plots 1 to -6 and toke the images by microscope respectively. To observe the dynamic evaporating process, we cut off the injecting tube of two phases and droplets were stopped in microchannel. At this time, an image of droplet was taken as the “0 min” image. After that, we toke the images every five minutes (figure 1b). In the other figures, the flow was not stopped, movies containing 50 frames of droplet images were captured at each point consequently, and then some frames were picked out randomly to analysis. In figure 2 and figure 4, 20 droplets were analyzed. In figure 3 and figure 5, 80 droplets were analyzed.

The droplet volume calculation out of the channel follows sphere’s volume formula. Given that the droplet in the channel is not spherical when droplet diameter is larger than the height of microchannel. In this case, we cannot calculate the droplet volume precisely. When the measured diameter of droplet is larger than 60um (twice that of the channel height), the volume is calculated by approximately considering droplet as cylinder [2].

$$V=\pi\left(\frac{D}{2}\right)^2\times h$$

D is the measured droplet diameter and h is the channel height.

When the measured diameter of droplet is in between 30 μm and 60 μm, the volume is calculated by approximately considering droplet as ellipse.

$$V=\pi\left(\frac{D}{2}\right)^2\times\frac{h}{2}$$

D is the measured droplet diameter and h is channel height.

Titanium oxide particle synthesis

The titanium sol was formed as described in another paper [1]. Briefly, 4 ml ethanol, 1ml acetic acid and 1ml tetrabutyl titanate were mixed together and stirred for 1-2min. The formed pale yellow solution was the titanium sol solution. In a flow focusing device, titanium sol droplets are formed stably and uniformly. After the sol droplet flow out channel, we collected and pipetted the droplet on a glass slide. Accompanied with solvent evaporating, sol droplet solidified into spheres. Then, we placed the glass slide with titanium spheres into a furnace and baked at 500 ℃ for 2 hours. The titanium oxide particles were formed. Due to the short working distance of the microscope, we can not observe submicrometer particles. To resolve this problem, we placed a cover lip on the surface of titanium oxide particles and inverted it on the microscope to observe the particles, as shown in figure S2.

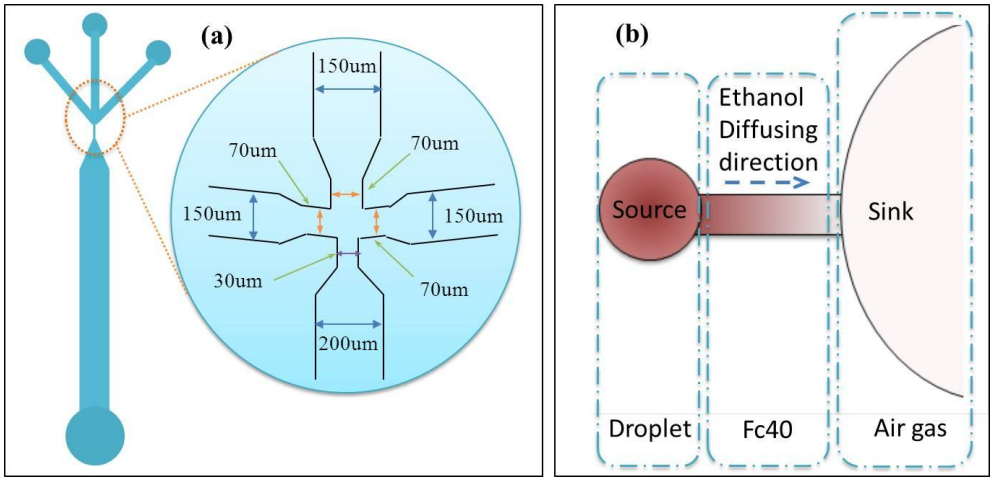

Figure S1. (a) Schematic of the designed microfluidic device, inset is the local magnification of orifice. (b) Model of the time-evolving concentration gradient. The source is the binary droplet (ethanol–water) and the sink is gas air.

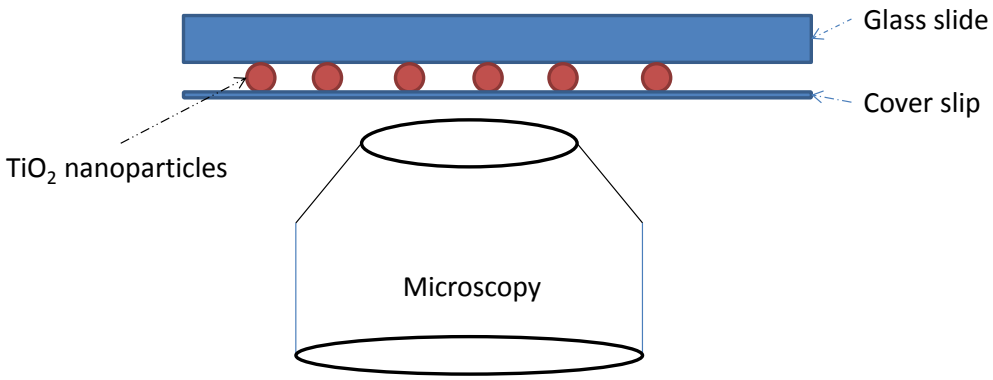

Figure S2. Schematic of titanium oxide nanoparticle observation under high magnification lens.

[1]. Zhaoxu Meng, Xu Zhang and Jianhua Qin, Nanoscale, 2013, 5, 4687–4690.

[2]. Shaojiang Zeng, Bowei Li, Xiao'ou Su, Jianhua Qin* and Bingcheng Lin*, Lab Chip, 2009, 9, 1340–1343.