A NOVEL MICROFLUIDIC CONCENTRATION GRADIENT DROPLET ARRAY GENERATOR FOR PREPARING OPTICAL ENCODING NANOPARTICLES

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ABSTRACT

This paper describes a multi-channel concentration gradient droplet array generator for preparing optical encoding nanoparticles. The device generated 64 groups of monodisperse droplets with the average diameter of 44 µm and RSD value of 5.5% (n = 64). Based on the concentration gradient droplet array generator, we synthesized 33 types of Au-Ag nanoparicles simultaneously with gradual shift of absorption spectra, which could be used as optical encoding nanoparticles for spectrometric applications.

KEYWORDS:
Concentration gradient, droplet array, Au-Ag nanoparicles, optical encoding.

INTRODUCTION

The optical encoding is an important spectrometric strategy for multiplex assays to track each reaction based on the absorption or emission spectrum of the encoding particles. [1] One of the most important challenges for multiplex assays is the limited spectra of encoding particles. Concentration gradient droplets can be used as micro-reactors for various synthesis and screening with low consumption and low diffusion, which should be a good choice for preparing optical encoding nanoparticles. However, the reported methods are usually deficient in high-throughput and simple operation. [2-3] The present device combines radial channel concentration gradient generation [4] with flow-focusing droplet generation to simultaneously form droplet arrays in parallel channels. Based the concentration gradient droplet array generator, we have synthesized optical encoding nanoparticles with dozens of spectra.

EXPERIMENT

The concentration gradient droplet array generator consists of three PDMS layers (Figure 1). The top layer includes a concentration gradient channel network (orange channels), partial oil channels (blue channels), flow-focusing constructions (pink triangle chambers) and droplet channels (pink channels). The concentration gradient channel network is mainly composed of 5 circular channels with serpentine branch channels surrounding each. The flow-focusing constructions are located at the downstream of the outmost serpentine channels. Two oil streams flow into each flow-focusing junction from both sides of each concentration gradient channel. The ends of 64 droplet channels are the outlets of the device. On the second layer, the oil is infused from a channel connected with a center chamber, and gradually distributed into the oil branch channels which are connected with the oil channels on the top layer via a series of access holes. The bottom layer is a substrate plate, which is bonded with the two other layers.

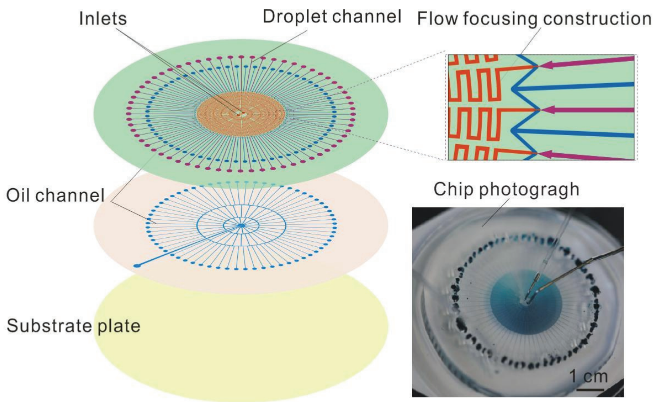

Figure 1. Schematic diagram and photograph of the concentration gradient droplet array generator

In this device, there are only two aqueous source solution inlets in the center and a single oil inlet at the edge. 64 outlets are located at the outmost side of the device for the simultaneous outflow of 64 groups of concentration gradient droplets.

RESULTS AND DISCUSSION

When two aqueous phase source solutions with different concentrations were introduced into the chip from the central inlets, they were distributed equally from circle channels into serpentine channels and mixed completely at the outlets of serpentine channels. After 5 times of distribution and mixing, the number of flow streams increased from two source solutions to 64 solutions. And two sets of 33 gradient concentrations between the two source concentrations were formed at the downstream of the outmost serpentine channels. At each flow-focusing junction, two oil phase streams introduced from the second layer sandwiched the aqueous phase solution into the focusing junction zone and sheared it into droplets. For the whole chip, an array of 64 concentration gradient droplets was generated simultaneously. The channels of two sets of concentration gradients were numbered 0 to 32 (32'). As the boundary channels, channel 0 and channel 32(32') delivered the two source solutions. Under these conditions, the measured gradient concentrations of the whole 64 droplet array were in accordance with the theoretical values (Figure 2), which show practically linear relationships with the code number of the outmost channels. The concentration value decreased by 1/32 step by step from channel 0 to channel 32 (32'), and the concentration gradient range of the droplet array was limited between the concentrations of the two aqueous phase source solutions.

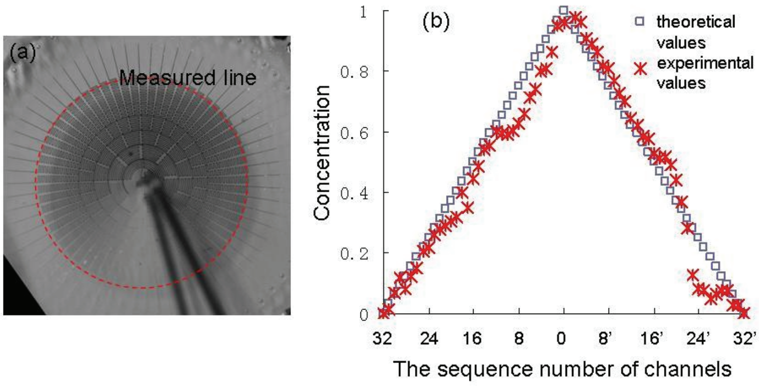

Figure 2. Concentration gradient of the droplet array (a) CCD image of the concentration distribution (b) Concentration gradient curves of the droplets (asterisk: measured value; square: theoretical value)

The size and mono-dispersivity of droplets were also discussed (Figure 3). At the flow-focusing junctions, 64 aqueous phase solutions with gradient concentrations were sheared into 64 groups of concentration gradient droplets by the oil phase at the same time. At a flow-rate of 2 µL/min for each aqueous phase and 24 µL/min for oil phase, the generation rate of droplet for the device was more than 5×10^4 droplets per minute. The average diameter of droplets is 44 µm with a RSD value of 5.5% (n = 64).

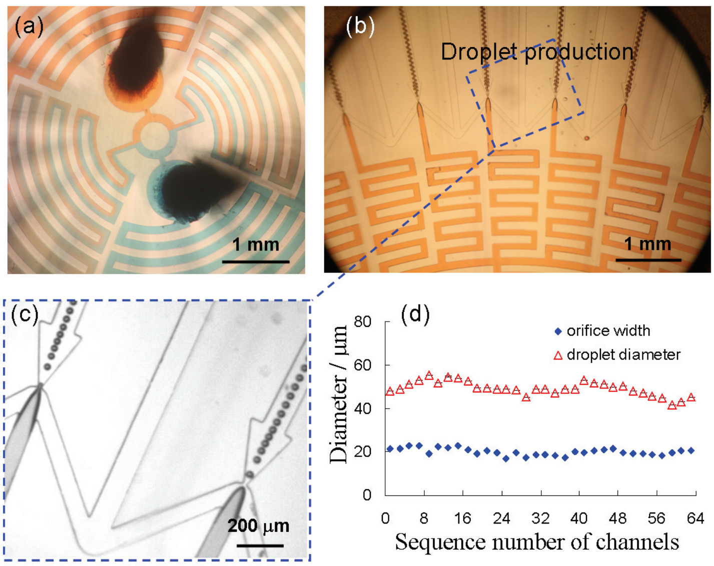

Figure 3. Droplet array generator (a) central concentration gradient channel network (b) droplet array (c) flow-focusing constructions (d) droplet diameter and orifice width in 64 channels

Using the concentration gradient droplets generated by the device as microreactors, gold-silver nanoparticles with 33 colors were prepared. As the Au/Ag molar ratio increased, the wavelength of maximum absorbance tended to increase. [5] To the best of our knowledge, this is the first to prepare Au-Ag nanoparticles with dozens of gradient molar ratio. The absorption spectra of Au-Ag nanoparticles were shown in Figure 4. As the molar ratio of gold and silver decreasing, the absorption band shifted from the pure gold nanopaticle spectrum to the pure silver nanoparticle spectrum. Though the values of absorbance are different, the trend of spectrum shifting is obvious. The Au-Ag nanoparticles can be used as optical encoding particles to immensely improve the number of color codes. Compared with that of 8-color quantum-dot-coated encoded silica beads [6], the theoretical code number of the Au-Ag nanoparticles increases from (n^8–1) to (n^{33}–1), which has great potential for high-throughput screening of multi-condition and multi-target.

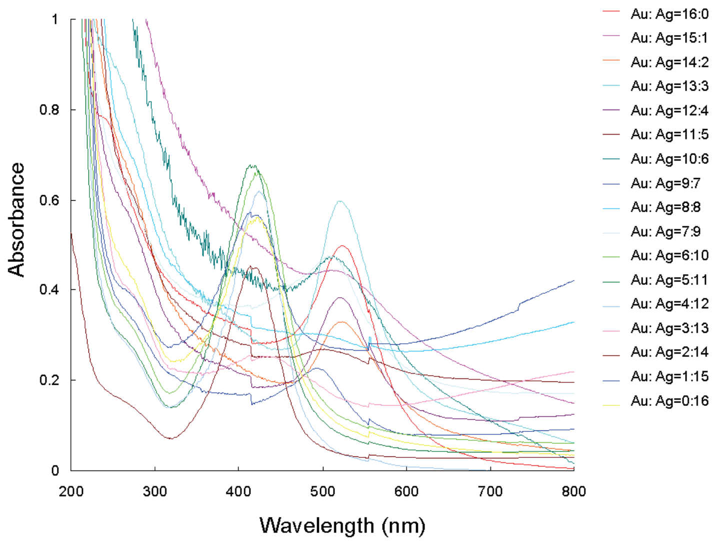

Figure 4. Absorption spectra of Au/Ag nanoparticles prepared on the concentration gradient droplet generator

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