

# SHAPE-CONTROLLABLE SYNTHESIS OF HYBRID STRUCTURES BY THREE-DIMENSIONAL (3D) HYDRODYNAMIC FOCUSING METHOD

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## ABSTRACT

We synthesized tetrathiafulvalene-Au (TTF-Au) materials by using three dimensional (3D) hydrodynamic focusing (HF) method. The 3D HF was achieved in a single-layer microfluidic device using a novel technique called “microfluidic drifting”. While keeping the flow rate ratio of the reagents as constant but changing the flow rates, the products showed different morphologies. Narrower size distribution was shown compared to the products prepared by vortex mixing.

## KEYWORDS

Microfluidic, Three-dimensional Hydrodynamic focusing, Shape-Controllable Synthesis

## INTRODUCTION

Nano and micro- structures synthesis has attracted increasing interest because of the widely application in various areas, such as biotechnology, medicine, optics, electronics, and so on. [1] Materials synthesis by using microfluidic method has shown its advantages such as reproducibility and high yields. [2] To further improve the monodispersity of products, uniform mechanical, chemical conditions, and reaction time are needed. This requires efficient mixing and uniform flow velocity in the reaction region. Two dimensional (2D) hydrodynamic focusing (HF) has been utilized to improve mixing efficiency and provide a horizontally uniform environment in the reaction region. [3] However, the variability of the flow velocity and chemical conditions in the vertical dimension increase the heterogeneity of the products. Besides, the physical contact of the synthesized particles with the channel wall will result in cross contamination and clogging of the devices. The 3D HF method confines the reaction region to a small volume at the center of the channel. Therefore, it provides uniform chemical and mechanical conditions in both the horizontal and vertical dimensions.

In our earlier work, we introduced a novel technique to manipulate fluid called “microfluidic drifting” to achieve 3D HF in a simple single-layer microfluidic device. [4,5] By using this device, we synthesized TTF-Au materials of different morphologies. Similar products of this reaction can be fabricated via bulk mixing while changing the ratio between the two reagents; however, this results in a broader size distribution.

## EXPERIMENT

Two reagents, 1 mM tetrathiafulvalene (TTF) and 0.27 mM hydrogen tetrachloroaurate (HAuCl<sub>4</sub>) in acetonitrile (ACN) were injected by syringe pumps via the two main inlets. At the sides, ACN was injected as buffer, as shown in Fig. 1a. Table 1. shows the flow rates used in each experiment. The 3D HF was accomplished in a two-step sequence. Firstly, reagent 1 was focused in the vertical direction by using the “microfluidic drifting” technique. At this step, due to a pair of counter-rotating vortices (Dean vortices) caused by the centrifugal effect in the 90-degree curve of the microfluidic channel, reagent 1 was shifted lateral to the middle plane of the channel. Then two horizontal focusing sheath flows (ACN buffer) further compressed reagents flow from both sides. Therefore, 3D HF is achieved with the combination of both steps and reagent 1 can be focused in the center of the microfluidic channel. [4]

The simulation of the 3D architecture of reagent 1 was carried out by using the computational fluid dynamic (CFD) simulation (CFDACE+, ESI-CFD), and the result is shown in Fig. 1. From sample a) to sample e), reagent 1 was focused in the center of the channel. For sample f), the flow pattern was different from other samples, but reagent 1 was still confined to a small region. Since the reaction only happens at the interface of the two reagents, the reaction region was confined with uniform chemical and mechanical conditions in both vertical and horizontal directions. Finally, the collected solution was concentrated using a centrifuge and dried on a clean silicon wafer for field emission scanning electron microscopy (FESEM) imaging.

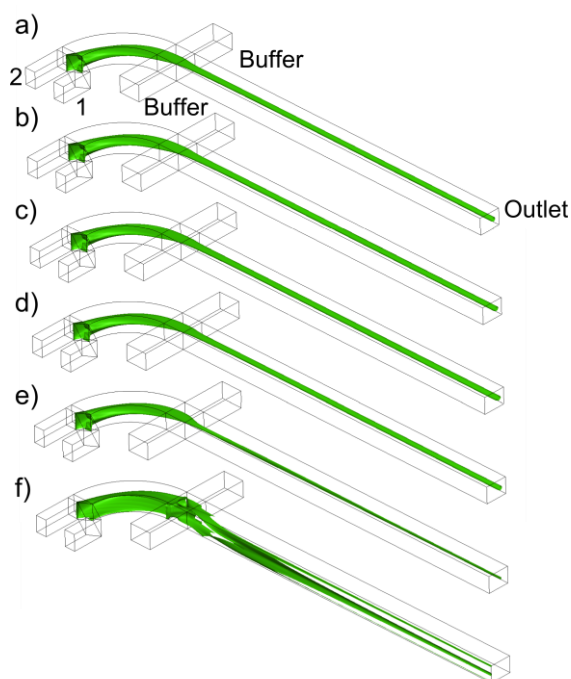


Figure 1. The CFD simulation of the 3D architecture of reagent 1 with the flow conditions in Table 1.

Table 1. Experiment Parameters

#	Reagent 1		Reagent 2		Buffer (ACN)
	flow rate ( $\mu\text{l}/\text{min}$ )	chemical	flow rate ( $\mu\text{l}/\text{min}$ )	chemical	flow rate ( $\mu\text{l}/\text{min}$ )
a	370	$\text{HAuCl}_4$	30	TTF	40
b	370	$\text{HAuCl}_4$	30	TTF	20
c	370	TTF	30	$\text{HAuCl}_4$	10
d	370	TTF	30	$\text{HAuCl}_4$	40
e	370	TTF	30	$\text{HAuCl}_4$	200
f	123.3	TTF	10	$\text{HAuCl}_4$	1000

## RESULTS AND DISCUSSION

Fig. 2 shows the SEM images of the materials fabricated by 3D focusing method. When TTF solution is focused in the microfluidic channel, tube and needle shapes were observed. As the flowrate of the buffer decreases, the structures become smaller, and shape changes from tube to needle shape. When  $\text{HAuCl}_4$  solution is focused in the microfluidic channel, the synthesized materials show particle-like shape. As the buffer flow rate increases, the size of the particles decreases, and the morphologies showed changes following the trend from branch, flower, multi-layers to triangle or hexagonal shape.

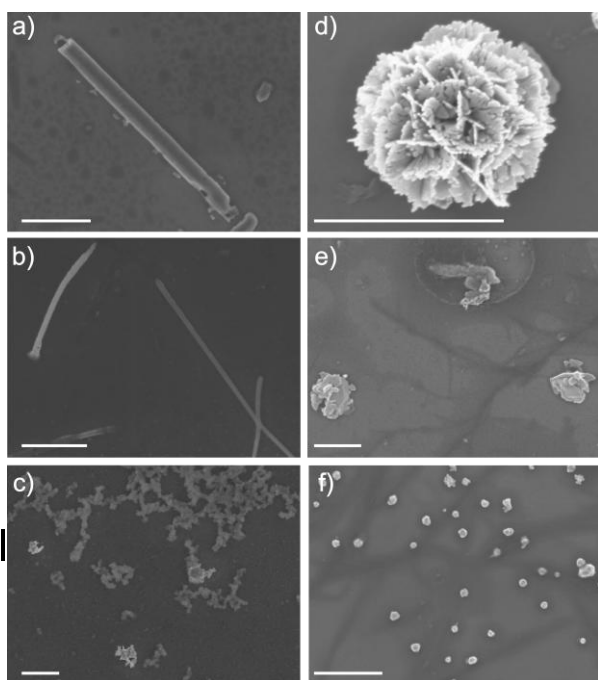


Figure 2. The SEM images of the structures fabricated by 3D focusing method. The scale bar size is  $1\ \mu\text{m}$ .

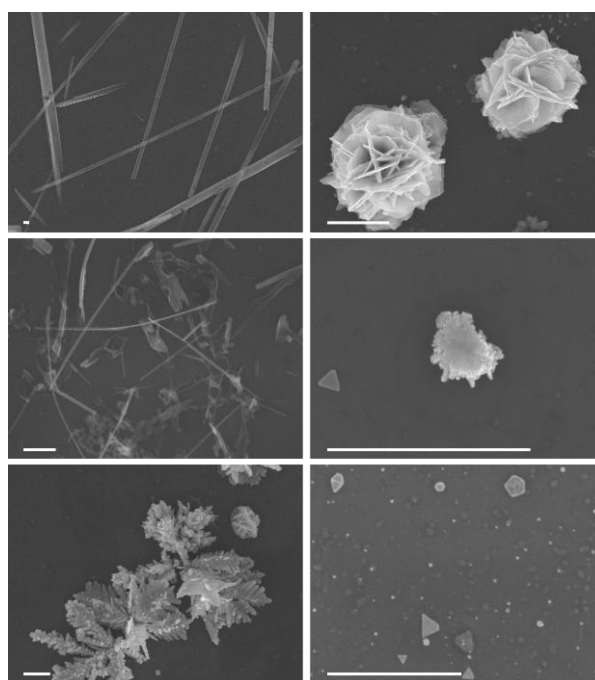


Figure 3. The SEM images of the structures fabricated by vortex mixing. The scale bar size is  $1\ \mu\text{m}$ .

The change of morphologies with the flow conditions in a two-dimensional (2D) focusing device was recently reported by J. Puigmartí-Luis, *et al.* [6]. However, the mechanism is still unclear. Here we tried to explain it by dividing the reaction into two steps: 1. inside and 2. outside the microfluidic channel. Because reagents flow in the channel for a limited time ( $< 50\ \text{ms}$ ), the reaction continues after flowing out the channel. The concentration and ratio of the reagents are different in step 1 and 2. During step 1, the reagents have not been diluted by the buffer yet. The reaction happens at the interface of two reagents, so the ratio between the two reagents is the ratio between the two original concentrations. During step 2, the ratio between the two reagents is the ratio between the total amounts of the two reagents in the solution, which is affected by the flow rates. As the result, the flow rate of buffer controls

the duration time of step 1, and different duration time of step 1 leads to different morphologies. Since this assumption is based on the change of the reagent ratio, we should be able to reproduce similar structures by changing the volume ratio of the two reagents by using vortex mixing method, as shown in Fig. 3. However, 3D HF method showed the advantages of producing products with narrower size distribution, as shown in Fig. 4. The size information was calculated from particles randomly chosen from SEM images.

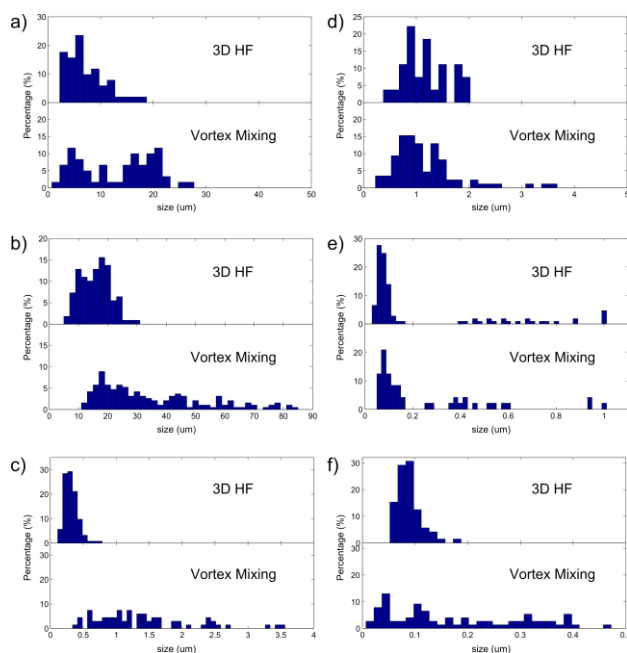


Figure 4. The size distribution of the product with different morphologies showed in Fig. 2 and Fig. 3.

## CONCLUSION

We synthesize TTF-Au structures by 3D HF using a simple single-layer microfluidic device based on “microfluidic drifting” technique. Different morphologies were achieved by tuning the flow rates, with smaller size distribution compared to conventional vortex mixing method. We believe this method can also be applied to synthesize micro and nano- structures of different materials, which will be widely used in diverse areas such as biotechnology, medicine, optics and electronics.

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