Time Resolve Study of Anisotropic Nanostructure Growth Using Integrated Droplet-Based Microfluidics and X-Ray Absorption Spectroscopy

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Abstract:

The objective of this project was to develop an integrated droplet-based microfluidic device, and study the structural evolution of nanomaterials during their synthesis within droplets via x-ray absorption spectroscopy and high-energy x-ray scattering. Flow-focusing microfluidic devices enable the formation of droplets with volumes ranging from nanoliters to picoliters at high frequencies (10 Hz to 10 kHz). These droplets behave as well-mixed batch reactors in which nanoparticle-forming reactions can occur. The high-frequency of droplet generation allows for large sampling sizes to determine the influence of system variables on the final nanostructure product. Our prototype microfluidic device was constructed out of polydimethylsiloxane (PDMS) using contact lithography, soft lithography, and plasma bonding to fabricate a PDMS microfluidic device bonded to a glass slide. Our first-generation device was unstable when generating droplets due to pressure fluctuations in the channels caused by debris removal filters. A re-design of the device enabled consistent droplet formation at variable flow rates of the continuous- and reactant-phase fluids at frequencies over 100 hertz (Hz). Currently we are incorporating resistive heaters and thermocouples onto the glass portion of the device for on-chip heating and temperature measurement. For future applications, the integrated device will be constructed entirely out of glass and x-ray transparent material for *in situ* x-ray analysis.

Introduction:

The mechanism by which nanomaterials assemble through processes, such as nucleation and growth, are presently undefine. Conditions for nanoparticle nucleation, crystallization, and growth normally require high temperatures and occur in a solution phase; thus they are difficult to study by *in situ* methods. This leads to the motivation of this project in which an integrated droplet-based microfluidic device compatible with x-ray analyses will serve as a platform to study the mechanism of nanoparticle formation.

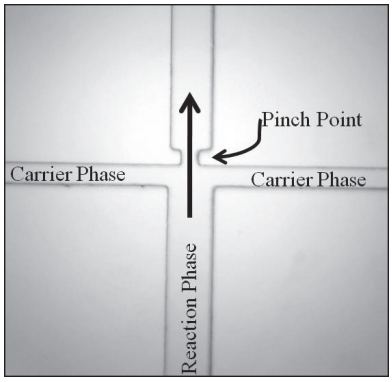

Figure 1: Flow-focusing junction allows for continuous generation of monodisperse droplets.

The use of a flow-focusing junction (Figure 1) induces droplet formation ranging with volumes on the order of nanoliters to picoliters with high frequencies (10 Hz to 10 kHz) [1]. Droplets generated within the device act as well-mixed batch reactors where nanoparticle-forming reactions occur. High-frequency droplet generation enables sufficient statistics to determine which system variables affect the nanoparticle structure. The application of microfluidic devices eliminates many of the inherent deficiencies of traditional reactors. The characteristic length of microfluidic devices is on the micron scale which encourages mixing times on the order of 1-10 μs [2]. The surface area-to-volume ratio of the channels coupled with the small thermal mass of the reactants (in comparison to the entire device) leads to rapid thermal equilibration. A well-mixed system with spatially defined temperature precincts facilitates precise process control. These well defined heating zones can be integrated directly on the devices.

Experimental Procedures:

The microfluidic device was constructed using photolithography coupled with replica molding by soft lithography. Transparency masks provided resolution of features as small as 10 μm, which was adequate for this application. SU-8-50 photoresist was spin-coated onto a

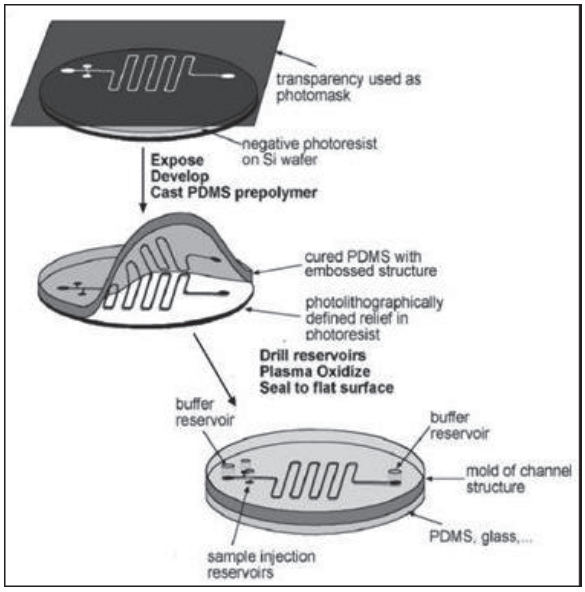

Figure 2: Droplet-generating microfluidic device fabricated by soft lithography [3].

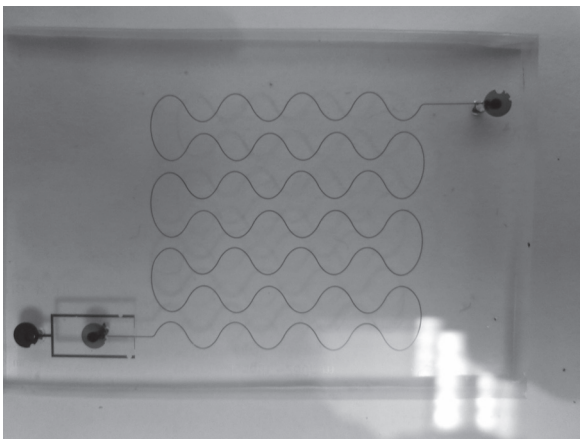

Figure 3: Photograph of a completed PDMS-glass device. The channels are filled with a black dye in order to contrast them against the PDMS.

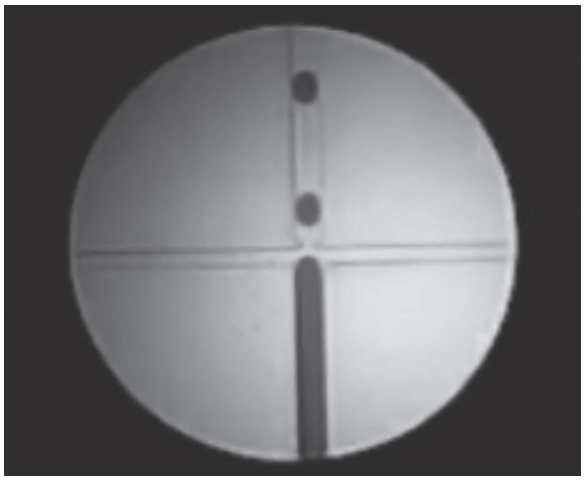

Figure 4: Consistent droplet formation in flow-focusing microfluidic device.

silicon <100> wafer followed by cross-linking under ultraviolet light exposure through the mask. The silicon substrate with the epoxy positive relief or "master" had channels with profilometry determined height of 69 ± 2 μm. A negative replica of the device was produced in PDMS by replica molding (Figure 2). The negative replica was separated from the master, and bonded to a glass slide using oxygen plasma (Figure 3). After exposure to oxygen plasma, the channels are hydrophilic due to hydroxyl groups formed on the PDMS and glass surfaces. This forms a covalent bond between glass and PDMS via condensation of hydroxyl groups. Since our continuous phase is perfluoromethyldecalin, we chemically modified the walls of the reactor with trichloroperfluorooctylsilane to ensure preferential wetting by the continuous phase. Small diameter polyethylene tubing was then inserted into the complete device to allow for independent syringe pump control of the continuous and reactant phases. By varying the relative flow rates of these two phases we can control the droplet size and generation frequency, allowing control over the nanoreactor characteristics.

Results:

The use of our first generation device proved to be unsuccessful. The first generation device was created with integrated filters to capture any particles (i.e., dust) that may have been pumped through the channels. These filters caused significant pressure fluctuations within the device which led to flow instabilities. These flow instabilities were significant enough that our microfluidic device was not capable of generating consistent droplets. As a result we re-designed the device, excluding filters which led to consistent droplet formation (Figure 4). Droplet volumes ranged from 1.4-4.0 nL and frequency generation from 14-116 Hz. The size of the droplets are determined by the ratio of the carrier phase to the reactant phase. A high carrier phase flowrate yields smaller droplets with higher frequency while a higher reactant phase flowrate yields larger droplets with lower frequency.

Future Work:

The final microfluidic device will be fabricated entirely out of glass with fully integrated on-chip heaters and resistance temperature detectors once a channel design is decided upon. Subsequently, metallic nanoparticle forming reactions will be studied in the newly constructed device to determine the effect reaction parameters have on size and shape. An all glass system will allow high temperature reactions and compatibility with *in situ* x-ray spectroscopy analysis.

Acknowledgements:

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References:

[1] Joanicot, M. et al. Science 2005, 309, 887.
[2] Solvas, X.C.I. et al. Anal. Chem. 2010, 82, 3950.
[3] Figure 2, Courtesy of the Whitesides Group.