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Unsteady Flow Simulations for Microchannel Design and Its Fabrication for Nanoparticle Synthesis

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Abstract**—**Micro-mixers play an important role in the lab-on-a-chip applications and micro total analysis systems to acquire the correct level of mixing for any given process. The mixing process can be classified as active or passive according to the use of external energy. Literature of microfluidics reports that most of the work is done on the models of steady laminar flow; however, the study of unsteady laminar flow is an active area of research at present. There are wide applications of this, out of which, we consider nanoparticle synthesis in micro-mixers. In this work, we have developed a model for unsteady flow to study the mixing performance of a passive micro mixer for reactants used for such synthesis. The model is developed in Finite Volume Method (FVM)-based software, OpenFOAM. The model is tested by carrying out the simulations at Re of 0.5. Mixing performance of the micro-mixer is investigated using simulated concentration values of mixed species across the width of the micro-mixer and calculating the variance across a line profile. Experimental validation is done by passing dyes through a Y shape micro-mixer fabricated using polydimethylsiloxane (PDMS) polymer and comparing variances with the simulated ones. Gold nanoparticles are later synthesized through the micro-mixer and collected at two different times leading to significantly different size distributions. These times match with the time scales over which reactant concentrations vary as obtained from simulations. Our simulations could thus be used to create design aids for passive micro-mixers used in nanoparticle synthesis.

Keywords**—**Lab-on-chip, micro-mixer, OpenFOAM, PDMS.

I. Introduction

IN recent years, Lab-on-chip (LOC) is an emerging research topic in health care industries. LOC is a miniaturization and combination of many technologies for applications such as chemical, clinical and bio-analytical system. Miniaturized LOC devices are also known as micro-total analysis system which has many applications specific to chemical synthesis of metals, semiconductor, inorganic and polymer nanoparticles [1]. Mixing in micro-mixer plays an important role in Lab-on–chips [2]. Also, they are used in fluid mixing, cell culture, enzyme reactor, heat exchanger etc. [3], [4]. Micro-mixing technology offers potential benefits to the future of chemical engineering and useful in relation to the time-scale of chemical kinetics. Diffusive transport in micro-devices is faster than in conventional mixers. Since mixing has a crucial impact on the overall performance of micro reaction processes, there is a need for measuring and comparing mixing performances [5], [6]. To explore the resulting potential, the mixing behavior of laminar flow mixers on micro-scales needs to be further investigated [7]. Numerical modeling and simulations are an integral part of such micro-device design. Over the last decade, many studies have been ended on steady flow of passive micro-mixing [8]-[11]. Considering the need of studying unsteady flows, we have developed such a flow model in OpenFOAM for investigating concentration variation on time scales during the process flow and its effect on the mixing performance. It was reported that "Y"-shaped micro-channel shows complete mixing at a shorter distance as compared to "T"-shaped micro channel in minimum mixing length [7], [12], subsequently for the validation of the model, we designed and fabricated "Y"-shaped micro-mixer in PDMS. The polymer based microstructures are mostly used in recent years. PDMS is a biocompatible and fast prototyping material [13]-[15].

In recent years, micro-mixers have emerged as an attractive technology for nanoparticle synthesis and are designed to manipulate fluids with reduced consumption of reagents [16]. The use of such micro-mixers gives the fine tuning property of synthesized nanoparticles. Nanoparticles are important to biomedical science as their critical size dimensions are close to the size of the cells, tissues, and micro-organisms etc. [17]. The rapid synthesis of nanoparticles with required size has great importance in the field of nanotechnology [18], which can be achieved using micro-mixers such as continuous flow micro-mixers or droplet micro-mixers [19]-[22]. In the present study, the fabricated Y micro channel structure was observed by an optical microscopy and initial testing was performed by passing two different dyes through the two inlets. The mixing performance was analyzed by processing the images in MATLAB and the mixing index is calculated. The Au nanoparticles were synthesized through the micro-mixer at 4 seconds and at the end of total flow time of 8 seconds. Au nanoparticles were characterized through UV-visible spectroscopy and field emission scanning electron microscopy (FESEM). Au nanoparticles of various sizes in the range of 24 nm to 64 nm were observed.

II. Numerical Model

A mathematical model to analyze the fluid flow and the concentration profile, in the micro channel is presented here.

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The model is based on continuum flow [23].

$$\frac{\partial c}{\partial t} + \overline{\nabla} \cdot \left(c\bar{v} \right) = D\nabla^2 c \tag{1}$$

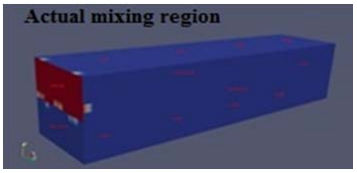
Assuming a current density for amount of active ingredient as:

$$c\bar{v} - D\overline{\nabla} c \tag{2}$$

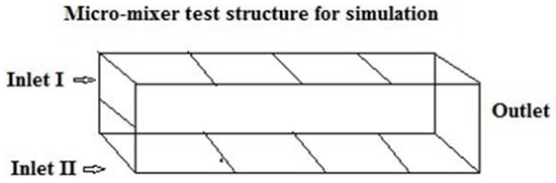
and invoking conservation of the active ingredient. c is the concentration of one of the phases and ṽ is the velocity field, and D is the diffusion constant. Further, we assume that the incompressible flow has reached a steady state for the velocity flow field. The momentum balance for such a flow would be expressed as:

$$\frac{\partial \bar{v}}{\partial t} + (\bar{v} \cdot \overline{\nabla})\bar{v} = -1/\rho \overline{\nabla} \mathrm{P} + \eta/\rho \nabla^2 \bar{v} \tag{3}$$

where, P is the pressure field and ρ is the density, and η is the dynamic coefficient of viscosity. We have assumed that Navier Stokes equations hold in the case of our two phase fluid.



(a)



(b)

Fig. 1 (a) Actual mixing region (b) Micro-mixer test structure for simulation

A versatile tool using OpenFOAM has been developed in order to simulate mixing efficiency in a simple micro mixer/reactor. In the present case, a Y shaped micro mixer with two inlets and one outlet, all having the same rectangular cross section, has been considered. The mixing variance along the length of the micro reactor with spatially varying boundary conditions (slip/no slip) has been simulated. (A structured mesh with cuboidal cells has been set-up of size 1000*1000* 40,000 micrometer). The mixing length of the channel is divided into four patches each of length 8725 micron which is placed on the top and bottom surfaces of the mixing length. It is important to note here that the side walls bear no slip conditions. The developed simulation tool can be used for low Reynolds number up to 10 and Péclet number up to 100. In the present case, we have considered mixing of two dyes. The micro channel geometry fixed is considered with two inlets and one outlet to study the mixing effect. A structured mesh with cuboidal cells of grading 10 has been set-up. A tool is developed using OpenFOAM C++ library directories viz. case, solver and utility by suitably engineering data structures contained in them. The information regarding the discretization (mesh), the values of parameters of PDEs and the side conditions were implemented in the case directory. The solver directory contains the data structures related to declarations of the flow fields and the partial differential equation along with the nature of side conditions. These were implemented using the mathematical model and customized for the application. The details of the numerical method used for discretizing the partial differential equation were implemented in the case directory. Similarly, data structures we are set up concerning the numerical technique for solving the resulting difference equations. Related details are described further. We employed Gauss linear and Gauss upwind schemes for gradient and divergence discretization in PDES of the mathematical model. Laplacian operators in the PDEs were truncated using the Gauss linear corrected scheme. Time derivative scheme was chosen to by Euler. Further, the difference equations that result, were numerically addressed using pre-conditioned conjugate gradient or biconjugate gradient techniques with smoothers available for pressure and concentration. Smooth solver technique was employed for the velocity difference equation and a symmetric Gauss Seidel smoother was used. The developed model helped to study the concentration distribution in the channel. Thus, the concentration distribution helps to study the mixing performance of the micro-mixer. Our model is useful for any type of micro-mixer geometry.

III. Experiment

A. Micro-Mixer Device Geometry and Fabrication

Fig. 2 Structural design of micro-mixer

The device was designed according to the dimensional parameters acquired after the simulation. The Y shape micro-mixer (100µm wide_20µm deep_40 mm long) has been fabricated having two inlets and an angle of 30^0 in between with one outlet reservoir having a diameter of 2 mm each.

A standard SU-8 process was used to fabricate a mold for the fabrication of a micro-mixer. The fabrication steps are schematically shown in Fig. 3 for the mold fabrication; SU-8 was spin coated at 1800 rpm for 30 s on a cleaned glass and then soft-baked at 95°C for 15 min. The soft-backed SU-8 was exposed to UV followed by a post-baking process. The SU-8 was then developed. The mold was salinized to enable the

removal of the PDMS chip from the mold after curing. The PDMS compound was prepared by mixing PDMS and its curing agent (by weight ratio 10:1). The fabrication was followed by degasifying the mixture. The mixture as then poured into the SU-8 mold and the mold was kept in an oven at 70°C for curing for a minimum of 1 h. The cured molded PDMS was peeled off from the mold and it was then bonded with glass by using oxygen plasma treatment [24], [25]. A fabricated micro-mixer is shown in Fig. 4 (a).

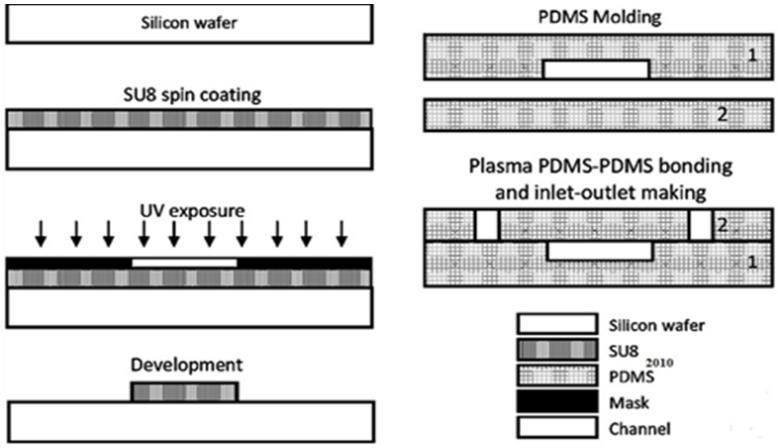
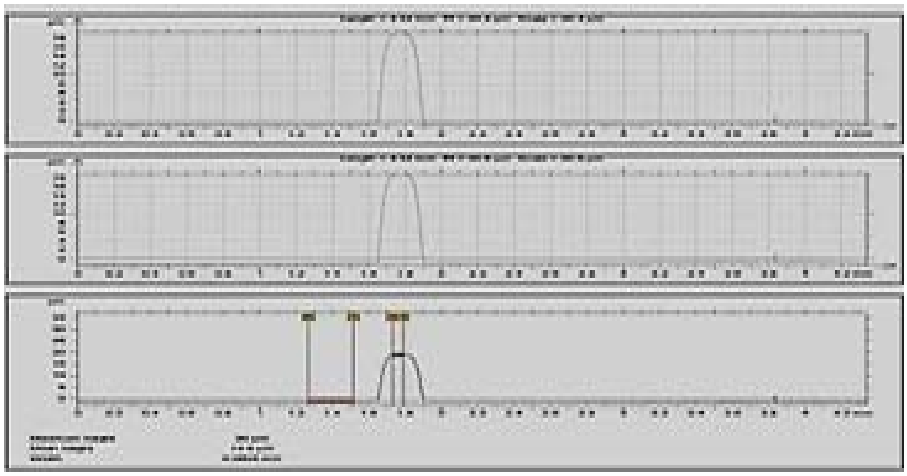


Fig. 3 Fabrication steps for PDMS micro mixer [26]

(a) Fabricated micro-mixer

(b) Mixing behavior of Y micro-mixer after filling with colors



(c)

Fig. 4 Fabricated PDMS Y micro-mixer (a) Before Assembling (b) after filling with fluids at Re=0.5 (c) Channel depth (20 μm) measured by Profilometer

The depth of the fabricated micro mixer shown in Fig. 4 (a) is 20 micron, measured by the profilometer. Photoresist SU-8 (2010) is used to fabricate the mold of the micro-mixer. The depth can be achieved further by using more viscous photoresist.

B. Experimental Procedure

To visualize the flow through the micro mixer, colored dyes were introduced as the mixing species into the two inlets. Specifically, blue and red dyes were used as the mixing flow

in experimental tests. Dyes were mixed at the flow rate of 0.001 ml/min using a programmable syringe pump (Harvard 11 plus, version 6.2). The syringes of diameter 4.6 mm were used along with infusion set of needles of 27G/19 mm size at the inlet reservoirs. Another syringe is used at the outlet to collect the mixed dyes. The mixed liquid obtained at the outlet was dark purple after mixing red and blue dyes; this was the indication of complete mixing. During the mixing process, several pictures were taken with a camera to evaluate the mixing index, as shown in Fig. 4 (b).

IV. Results and Discussion

In this study, a simple Y-type micro-mixer (shown in Fig. 1) is the design of actual fabricated passive micro-mixer used for experimental work. Mixing is investigated through the simulation model by concentrating plots across the micro-mixer at different cross sections as well as by calculating the mixing index at various cross sections. Similarly, the results were validated fabricating the actual micro-mixer.

A. Simulation Results

The simulation results are shown in Figs. 5 (a)-(c), as below. Cross sections are taken during simulation at different locations along the x-axis of the micro-mixer. Mixing of the two chemical phases can be observed through these cross sections.

(a) Cross section I (b) Cross section I (c) Cross section III

Fig. 5 Simulated mixing images (a) Cross sections I taken at 1300 µm (a) Cross sections II taken at 2600 µm (c) Cross sections I taken at 4000 µm

The cross-sectional concentration distributions are also taken during the simulation process to demonstrate the mixing characteristics along the downstream channel. These three cross sections show that the mixing of two species is increasing along the length of the micro-mixer.

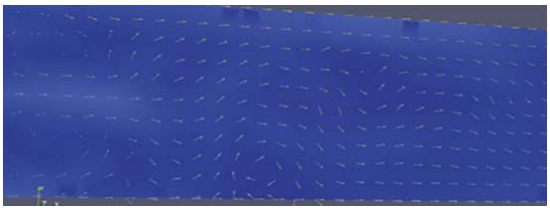
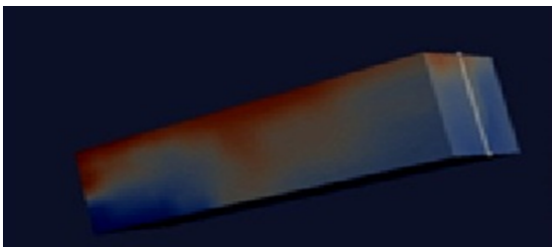
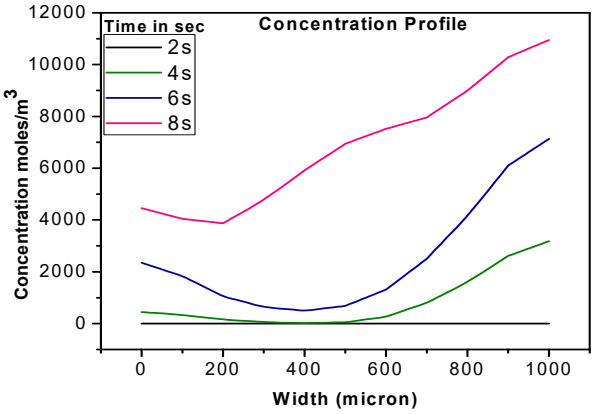


Fig. 6 Velocity magnitude profile and the transversal flow through micro-mixer

Fig. 6 shows that the fluid near the center experiences a centrifugal force due to which cross flows are generated. The highest fluid velocities along the central axis progresses mixing of the two colors until it reaches to the outlet. Introducing some geometric variations will generate more vortices in the active length of the micro-mixer and will result in increased mixing performance. Our developed model can be used to study the concentration profiles for any geometry just by varying the velocity boundary conditions.



(a)



(b)

Fig. 7 (a) Simulation domain at the end of flow time (b) Concentration profiles at various time scales at the outlet of the micro-mixer

Fig. 7 (a) shows visual effect of mixing of two fluid phases obtained during simulation. Fig. 7 (b) shows plot of concentration profile along a vertical line segment at the center of the exit of the cuboidal region (spatial flow domain) at various time scales of the process flow time. The concentration profiles thus obtained are called line segment profiles. The plot at the start of the flow i.e. at 2 seconds, shows no mixing of the fluids, then at 4 seconds, the fluids started interfering with each other. The flat part in the middle of the graph shows prominent mixing at the end of the flow time i.e. at 8 seconds. It indicated the stability of the flow at concentration of 8000 mole/m^3. Concentration data of the line profile of all the cross sections is evaluated to study the mixing index using the formula given in (4) presented in Table I.

$$\sigma = \frac{1}{c_\infty}\sqrt{\sum_{i=1}^{N}(c_i - c_\infty)^2 / N} \quad (4)$$

σ - Mixing Variance, N- Sample Points, c_i - Reference concentration value, c_∞ - Maximum concentration value.

(a) Cross section I (b) Cross section II (c) Cross section III

Fig. 8 Experimental mixing images (a) cross sections I taken at 1300 µm (b) Cross sections II taken at 2600 µm (c) Cross sections I taken at 4000 µm

B. Experimental Results

1. Image Processing using MATLAB: To study the mixing performance and to find out the mixing index, the vision based method is used. Cross sectional images from the composed mixed color were cropped for the processing shown in Figs. 8 (a)-(c). The MATLAB tool was used to process these images. These images were in RGB plane which were converted to HSV plane. The, the images were segmented and the mixing index calculated by using the standard deviation method as per the formula given in (5) and presented in Table I.

$$\sigma \equiv \frac{1}{N}\sum_{i=1}^{N}\sqrt{(I_i - I)^2} \quad (5)$$

σ - Mixing Variance, N- Sample Points, I_i- Reference Intensity value, I- Maximum Intensity value.

2. Validation of Simulation and Experimental Results:

TABLE I
COMPUTED MIXING VARIANCE AND MIXING INDEX AT DIFFERENT CROSS SECTIONS OF THE MICRO-MIXER

Cross section Location (µm)	Mixing variance (moles/m^3) simulated	experimental	Mixing index simulated	experimental
1300	836	736	0.94	0.83
2600	548	508	0.97	0.87
4000	205	190	0.98	0.89

C. Synthesis of Gold Nanoparticles (AuNPs) in a Microfluidic Environment

Having developed and validated a simulation tool for mixing of two reactants in micro channel, we now turn to the engineering application of nanoparticle synthesis. We consider AuNPs as they have been particularly studied widely in the literature. In general, AuNPs are synthesized in a macro-scale environment (in batch) with heating the mixed solution. The main advantage of macro-scale reduction is the complete mixing of the reactants i.e. gold precursor (gold salt) and sodium citrate. However, miniaturization of the reaction platforms provides new opportunities for advanced synthesis properties [24]. In particular, synthesis can be completed in the absence of any heat source. A schematic of the synthesis in a micro-mixer is shown in Fig. 10.

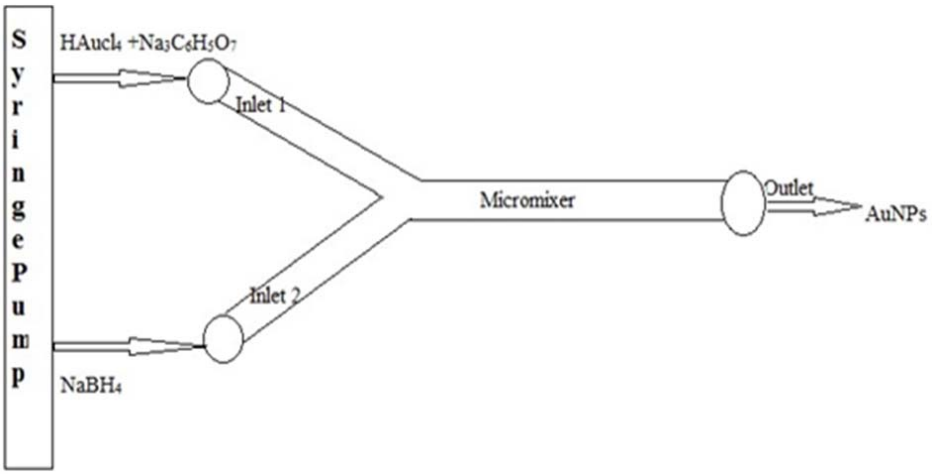


Fig. 9 Schematic of Synthesis of AuNPs in a micro-mixer

D. Synthesis of AuNPs Using the Fabricated Micro-Mixer

Reagents: Trisodium citrate ($Na_3C_6H_5O_7$), Sodium borohydride ($NaBH_4$), gold chloroacuric acid ($HAucl_4$).

To synthesis nanoparticles, the reactants were loaded in two streams. Solution of 10 ml of 0.002 M $HAucl_4$ (gold chloroacuricacid) and 10 ml of 0.001 M of Na3C6H5O7 (Trisodium citrate) was prepared. This solution was introduced into the first stream, while 0.01 M of $NaBH_4$ was introduced into the second stream. The flow rate of 0.001 ml/min was selected. Formation of Au nanoparticles was indicated when light pink color solution was observed during mixing in a micro-mixer after introducing these solutions through the two inlets. The mixed homogeneous solution was collected at the outlet at 4 seconds and 8 seconds, respectively, where we subsequent to the process below, observed a major difference in size distribution of NPs. The mixed AuNP

solution is taken on the silicon wafer for characterization. The size distribution of these particles was obtained through SEM images and analyzed from the UV/V is absorption spectrum. Figs. 11 (a) and (b) represents the FESEM images of the gold nanoparticles obtained in micro-mixer. Particles in spherical shape with relatively diameter ranges from 24 nm to 62 nm were observed by FESEM.

1. Characterization of Gold Nanoparticles

Samples are characterized by UV visible spectroscopy and by field emission scanning electron microscopy (FESEM) where gold nanoparticles of different sizes are observed.

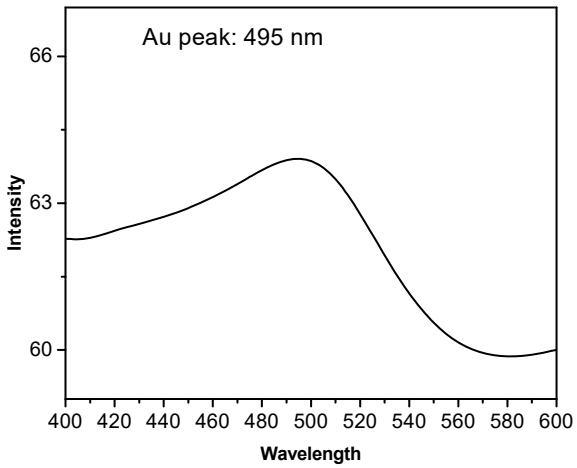


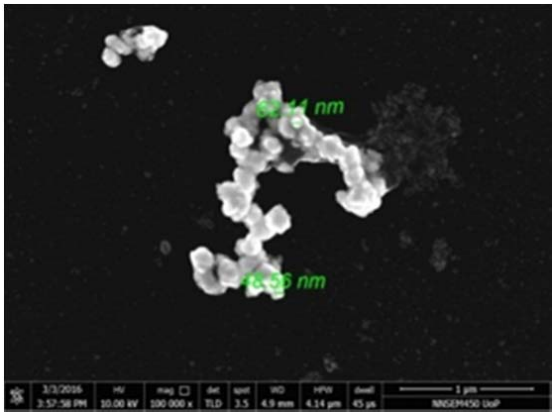
Fig. 10 UV visible spectroscopy result

The optical absorption spectra in Fig. 10 indicate that synthesized nanoparticles have surface plasma resonance peak at 495 nm.

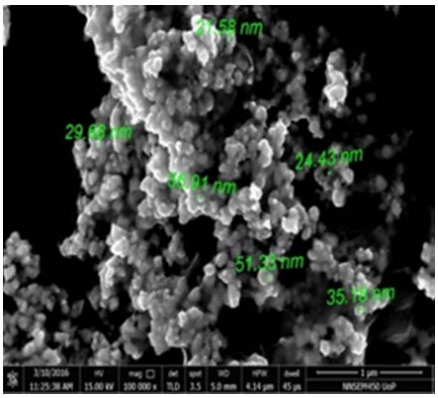
The nanoparticles collected at 4 seconds of the flow time were shown in Fig. 11 (a) having the size of 48 nm to 65 nm. The NP collected at the end of the flow time i.e. 8 seconds, as in Fig. 11 (b), were more in number and of various sizes from 24 nm to 51 nm. Thus, the simulation time along with the concentration of the reactants is an important factor in microfluidic nanoparticle synthesis. We note that the time scales of unsteady simulations of reactant mixing match with the time scales at which significantly different size distributions were experimentally obtained.

V. Conclusion

We propose that the designs of passive micro-mixers used for nanoparticle synthesis need to be optimized by developing unsteady flow models for reactants. Size distribution of NPs, an important performance parameter relates to concentration profiles of reactants in such a device. We obtained time scales of concentration profile variation from simulations of a Y type micro-mixer design and compared them with time scales of variation in size distributions of AuNPs experimentally synthesized using such a design. We thereby show that unsteady flow simulations would be critical for understanding this relation. Before carrying out this experiment, the simulation model was validated using two color dyes in the fabricated micro-mixer.



(a)



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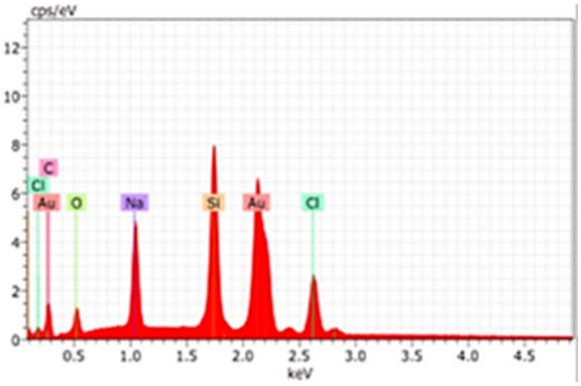

(c)

Fig. 11 (a) Gold nanoparticles obtained at 4 seconds of flow time, (b) Gold nanoparticles obtained at the end of flow time (8 seconds), (c) EDS results of FESEM

We further suggest that flow time could be used as an important parameter for nanoparticle synthesis after studies relating concentration profiles to size distributions. As a part of future work, we also propose to engineer boundary

conditions of velocity to achieve concentration profiles and study their effects of experimental validation upon nanoparticle size distribution.

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