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Size Control of Nanoparticles Using a Microfluidic Device

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***Abstract*—**We have developed a microfluidic device system for the continuous producing of nanoparticles, and we have clarified the relationship between the mixing performance of reactors and the particle size. First, we evaluated the mixing performance of reactors by carrying out the Villermaux–Dushman reaction and determined the experimental conditions for producing AgCl nanoparticles. Next, we produced AgCl nanoparticles and evaluated the mixing performance and the particle size. We found that as the mixing performance improves the size of produced particles decreases and the particle size distribution becomes sharper. We produced AgCl nanoparticles with a size of 86nm using the microfluidic device that had the best mixing performance among the three reactors we tested in this study; the coefficient of variation (*Cv*) of the size distribution of the produced nanoparticles was 26.1%.

***Keywords*—** Microfluidic, Mixing, Nanoparticle, Silver Chloride.

I. Introduction

MICROMACHINING techniques have been adopted in the design of miniaturized devices, e.g. microfluidic devices, for chemical synthetic applications [1]-[3]. A microfluidic device is a reactor in which chemical reactions can be performed carried out on a microscale [4], [5]. The potential advantages of using a microfluidic device, rather than a conventional batch reactor, are as follows: the temperature can be controlled effectively in a microfluidic device; the fluids to be mixed have a laminar flow, and mixing progresses rapidly because of the short diffusion length of the materials in the microfluidic device.

Because of these advantages, recently, microfluidic devices have been used in the field of nanotechnology. We can produce nanoparticles using a microfluidic device by controlling nucleation, particle growth, and aggregation. Since rapid and uniform mixing can occur in a microfluidic device in the nucleation stage, the duration of the particle growth stage can be kept constant. Therefore, uniform particles can be continuously produced.

The production of fine nanoparticles using a microfluidic device has been reported in many papers. For example, Maki et al. [6], produced Au nanoparticles using microfluidic devices under various conditions, e.g., for different concentrations, residence times, and types of microfluidic devices. Thus, they were able to effectively control the size of the produced Au nanoparticles.

Lin et al. [7] produced monodisperse Ag nanoparticles using a continuous flow tubular microfluidic device. They found that the Ag nanoparticle size distribution broadened with an increase in the residence time of the temperature.

Yang et al. [8] prepared hydroxyapatite (HAP) nanoparticles using three types of microfluidic devices. They reported that the particle size and the particle size distribution depended on the flow rate, the mixing distance, and the type of microfluidic device used.

However, in the above mentioned studies, few studies have involved an evaluation of the relationship between the mixing performance of a microfluidic device and the particle size. Therefore, the objectives of this study were to design a microfluidic device system and to produce small and uniform AgCl nanoparticles using the microfluidic devices developed in this study.

II. Experimental Method

A. Evaluation of the Mixing Performance

To evaluate the mixing performance of the reactors, we selected the Villermaux-Dushman reaction [9], [10], which is represented by (1)-(3) and shown in Fig. 1. Reaction (1) is an acid-base reaction, and reaction (2) is a reduction-oxidation (redox) reaction. These reactions are parallel competing reactions.

$$CH_3COO^- + H^+ \rightarrow CH_3COOH \quad (1)$$

$$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (2)$$

$$I_2 + I^- \rightarrow I_3^- \quad (3)$$

III. Microfluidic Device System

A. Laboratory System

Fig. 1 shows the Micro Process Server™, a laboratory microfluidic device system produced by Hitachi Plant Technologies, Ltd. The Micro Process Server™ consists of a flow control part, the temperature control part, and a microfluidic device.

B. Microfluidic Device

This microfluidic device consists of a housing and a chip in which multilayer flow occur. In this study, we used two kinds of microfluidic devices in which the channel width and the number of flows were different, as shown in Fig. 1. We evaluated the mixing performance using two parameters, as shown in (4) and (5).

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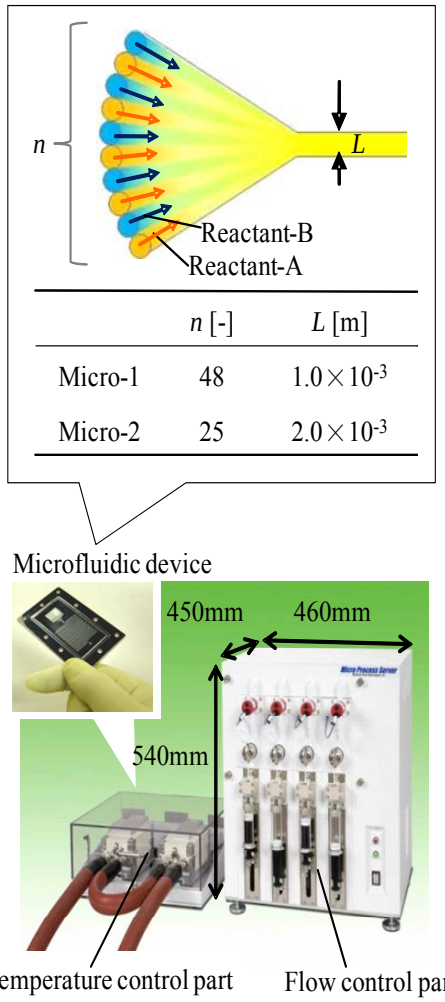
$$U = \frac{2Q}{\pi} \cdot \left(\frac{2}{D} \right)^2 \quad (4)$$

$$L = \frac{D}{n} \quad (5)$$

Here, U is the mean fluid velocity, Q is the volumetric flow rate of reactant A or that of reactant B, D is the diameter of the PTFE tube of reaction part, L is a characteristic liner dimension, and n is a number of flows.

C. Conventional Batch

We performed experiments using the conventional batch method to compare with microfluidic devices. The detail specification of batch method is as shown in Fig. 2 and Table I.



	n [-]	L [m]
Micro-1	48	1.0×10^{-3}
Micro-2	25	2.0×10^{-3}

Fig. 1 Laboratory microfluidic device system

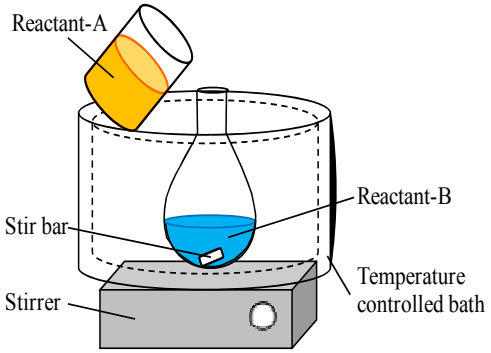


Fig. 2 Conventional batch system

TABLE I
SPECIFICATION OF BATCH METHOD

Capacity of vessel [m^3]	1.0×10^{-4}
Rotational speed of stirrer [s^{-1}]	15
Quantity of mixture [m^3]	4.0×10^{-5}

IV. PRODUCTION OF NANOPARTICLES

We selected a reaction that yielded silver chloride (AgCl) nanoparticles from silver nitrate ($AgNO_3$) and sodium chloride (NaCl), as shown in (6). Table II lists the experimental conditions.

$$AgNO_3 + NaCl \rightarrow AgCl + Na^+ + NO_3^- \quad (6)$$

$AgNO_3$ and NaCl solutions with a molarity of 5.0×10^{-2} kmol/m^3 were prepared. Equivalent amount of these solutions were introduced and mixed in a micro fluidic device of a Micro Process Sever™ as shown in Fig 1. To inhibit aggregation, a polyvinylpyrrolidone (PVP) solution with a molarity of 1.0×10^{-2}kmol/m^3 was prepared and was mixed with an equal quantity of the product solution.

The particle size distribution was evaluated using the coefficient of variation (Cv) as shown in (7).

$$Cv = \frac{100\sigma}{\overline{\varphi}} \quad (7)$$

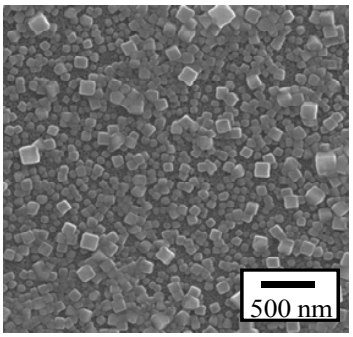
Here, σ denotes the standard deviation and $\overline{\varphi}$ denotes the average particle size.

TABLE II
EXPERIMENTAL CONDITIONS FOR PRODUCTION OF NANOPARTICLES

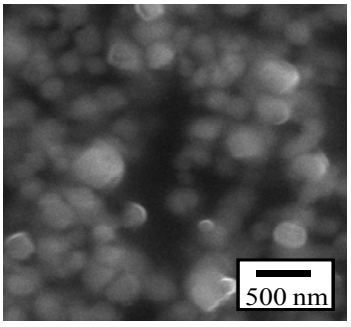
Molar concentration [kmol/m^3]		
Reactant-A	$AgNO_3$	5.0×10^{-2}
Reactant-B	NaCl	5.0×10^{-2}
Flow rate [mm^3/s]		
Reactant-A		16.7-66.7
Reactant-B		16.7-66.7
Temperature controlled bath [K]		293.15

Fig. 3 shows the experimental results for the three reactors. The size of the particles produced by using Micro-1 was 86.9

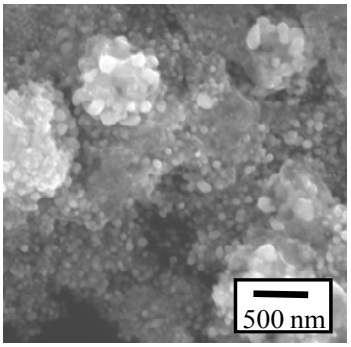
nm and *Cv* was 26.1%, as shown in Table III. Because the mixing performance of Micro-1 was better, one-to-one reaction between the AgCl and NaCl molecules occurred, and nanoparticles were produced immediately. On the other hand, when Micro-2 was used, the particle size was 123.3nm and *Cv* was 48.2%. Further, when the batch method was used, particle size was 207.6nm and *Cv* was 55.0%. Since the mixing performance was poor and nanoparticles were not produced immediately. In addition, the batch method could not be controlled by mixing and reaction. Further, the processes of nucleation and particle growth occurred simultaneously in the vessel.



(a) Micro-1



(b) Micro-2



(c) Conventional batch

Fig. 3 SEM photographs of the AgCl nanoparticles

TABLE III
COMPARISON OF THE SILVER CHLORIDE NANOPARTICLES SIZE AND THE DISTRIBUTION BETWEEN THREE REACTORS

	Micro-1	Micro-2	Batch
Particle size [nm]	86.9	123.3	207.6
Cv [%]	26.1	48.2	55.0

As a result, we observed a correlation between the mixing performance of reactors and the particle size of product; thus, we concluded that better mixing performance results in the production of smaller particles and a sharper particle size distribution. From SEM (Scanning Electron Microscope) images, we confirmed that the nanoparticles produced by the batch method aggregated; on the other hand, the nanoparticles produced in the microfluidic devices did not form aggregates and were dispersed.

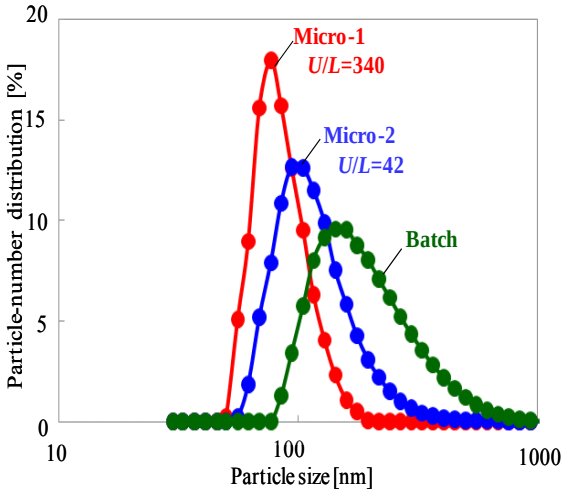


Fig. 4 AgCl Nanoparticle size distribution evaluated by a laser diffraction particle size analyzer

V. CONCLUSION

We produced AgCl nanoparticles using a microfluidic device and evaluated the mixing performance and the particle size. It was found that the size of produced nanoparticles decreased and the particle size distribution became sharper when the mixing performance was improved. We produced AgCl nanoparticles with a size of 86nm using the microfluidic device that had the best mixing performance; the coefficient of variation of the size distribution of the produced nanoparticles was 26.1%.

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