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Re-Dispersion of Flocculated Nanoparticles Using Back Pressure Valve with Small Orifice Channel

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Abstract– Nanoparticles tend to flocculate owing to their high surface energy. Flocculated nanoparticles can cause a loss of properties and problems when used in applications. This paper describes an easier and more effective method for producing a colloidal solution in which flocculated nanoparticles become re-dispersed by using a back pressure valve. First, we identify the mechanism of re-dispersion in this valve from simulations integrating the shear force and the van der Waals attractive force for a nanoparticle solution with a Couette flow. From the results, shear stress dominates the re-dispersion of flocculated particles. In experiments, a large shear stress is applied to the solution in a back pressure valve for re-dispersing the flocculated particles. The clearance of the flow path in the valve decreases with increasing primary pressure. The re-dispersibility is evaluated through the measurement of their size distribution using dynamic light scattering. The results show that the method re-dispersed the flocculated particles and reduces their modal diameter from over 6000 nm to 21.0 nm. Additionally, increasing the pressure decreases the particle diameter after the re-dispersion. Moreover, we can predict the particle diameter after the re-dispersion from the dispersion numbers *Di* (the ratio of the shear force to the van der Waals attractive force).

1. Introduction

Nanoparticles are used extensively as materials in medicine, plastics, energy, and electronics industries [1]. For nanoparticles with diameters on the order of a few nanometers (single-nanometer), the surface properties and particle interactions are much more significant than those of bulk materials. Low electrostatic repulsion leads to flocculation of nanoparticles [2]. Flocculated nanoparticles can cause a loss of properties and problems when used in applications. For example, in a medical diagnostics, flocculated fluorescent nanoparticles have low definition during image acquisition for diagnosis or distribution. It is, therefore, important to maintain the nanoparticles dispersed in solutions. As a way to disperse flocculated nanoparticles, we used a milling apparatus using media such as balls, beads, and sand [3]. These apparatuses apply stress for the re-dispersion of flocculated nanoparticles. Mechanical dispersion apparatuses have been developed and can decrease the re-dispersed particle diameter [4]. During the procedures, however, such an apparatus requires complicated operation including separation of the media (balls, beads, and sand) from the solution and washing of the media. Furthermore, no apparatus has been found to reduce the particle diameter to the order of primary particle diameter. A high pressure homogenizer has also been proposed as an apparatus not using a media [5,6]. However, the clogging in the narrow micrometer size ducts is a disadvantage. Thus, to re-disperse flocculated nanoparticles with the desired function, we need to develop a new apparatus.

This paper describes an easier and more effective method for producing a colloidal solution in which flocculated nanoparticles become re-dispersed by using a back pressure valve [7]. The clearance of the valve is adjusted with a spring. Therefore, the valve is prevented from clogging and easy to wash. In the clearance of back pressure valve, the shear stress depending on pressure drop is applied to flocculated particles. We use the shear stress for the re-dispersion. From the simulation and experimental results, we also have identified the re-dispersion mechanism and established a prediction method of re-dispersed particle size in this apparatus.

2. Simulation to confirm the effectiveness of shear force for nanoparticle re-dispersion

First, we confirmed the effectiveness of shear force on the nanoparticle re-dispersion. Fig. 1 shows the results of simulations using by SNAP-F (Structure of NAnoParticles-Flow, Ver. 3.1.1, Meso-Simulation Consortium). In this simulation, nanoparticles and water are confined between parallel plates. The individual particle size was set at 30 nm, and the distance between the plates was 210 nm. The time step was 10^{-10} s. The plates move opposite directions. The move generates Couette flow and shear in the channel. The bottom graph shows the number of particles included in a flocculated particle over time. The number decreases over time, and this tendency is enhanced with increasing wall moving velocity, that is, shear force. Thus, the flocculated nanoparticles are re-dispersed to smaller group of particles with high shear force. Then, we conducted the re-dispersion experiment using a back pressure valve.

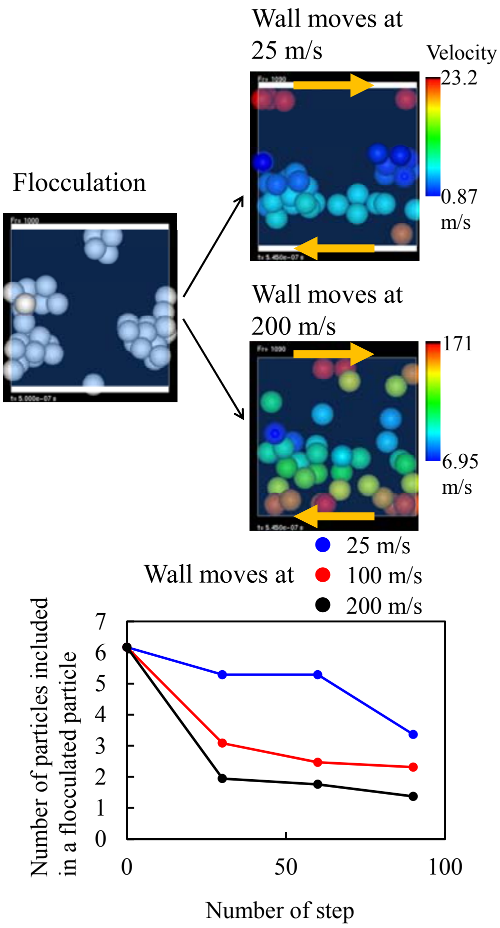

Fig. 1 Simulation results of particle dispersion by shear force.

3. Experimental

3.1. Materials and Method

As a sample of flocculated nanoparticles, we use CdSe/ZnS-core/shell QDs surface modified by (2S)-1-[(2S)-2-methyl-3-sulfanylpropanoyl] pyrrolidine-2-carboxylic acid (captopril). The captopril modified QDs are nanoparticles with medical applications in drug delivery and diagnosis.

For the development of an apparatus that can re-disperse flocculated nanoparticles, we have designed an apparatus that incorporates a back pressure valve. The back pressure valve can control the shear stress applied to the flocculated nanoparticle solution by setting the pressure drop. Fig. 2 shows a continuous process for nanoparticle re-dispersion (top) and a schematic of the back pressure valve included in the process (bottom). The valve can control the primary pressure up to 35 MPa. Through this process, we can obtain clear nanoparticle solution owing to the nanoparticle re-dispersion. Since the pressure after the valve is atmospheric and the primary pressure is shown by the gauge pressure, the primary pressure shown by the pressure gauge is equal to the pressure drop.

The flocculated QD-cap (modal diameter is more than 6000 nm) were re-dispersed through the feed of the solution to the back pressure valve (denoted by BPV in Fig. 2, HPB-450, AKICO Co.) under the primary pressure of 1–35 MPa using a high pressure pump (NP-D-324, Nihon Seimitsu Kagaku Co. Ltd.). The flow rate of the solution was set to 5.2 mL/min. The bore diameter at the clearance of the back pressure valve was maintained with a spring and decreases with increasing the primary pressure. The internal diameter (i.d.) of the inlet channel (3 mm) narrows to 1 mm in the back pressure valve, and then further narrows to the bore diameter of the clearance corresponding to the primary pressure. After the clearance, the pressure suddenly returns to atmospheric pressure, and the solution flows into the duct of 2 mm i.d. and finally the outlet channel of 3 mm i.d. The residence time in the process was 1 min.

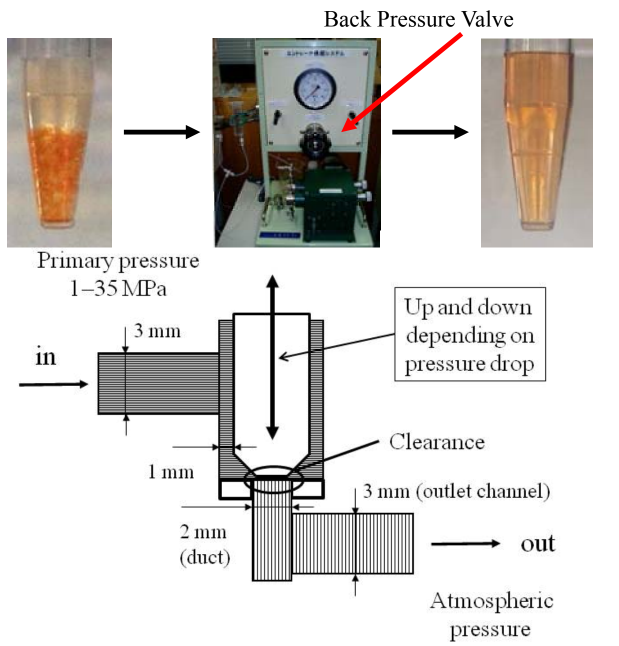

Fig. 2 Re-dispersion process including a back pressure valve.
Top: Photograph of the process and nanoparticle solution.
Bottom: Schematic of the back pressure valve.

3.2. Results and Discussion

Table 1 shows the re-dispersibility of the valve for various pressure drops. The increase in the pressure drop decreased the particle diameter after the process. The modal particle diameter right after the synthesis was 13.5 nm. The re-dispersed nanoparticle size is on the same order of that of the initial particle. In this way, the treatment through the back pressure valve re-dispersed the flocculated QD-cap from more than 6000 nm to less than 100 nm. The experiment also validates the effectiveness of the shear force on the re-dispersion of flocculated nanoparticles.

Table 1 Re-dispersibility with various pressure drops

Pressure drop	Modal diameter [nm]	Mean diameter [nm]
1 MPa	43.8	98.3±4.1
3 MPa	32.7	82.7±2.9
35 MPa	21.0	44.3±1.7

Table 2 Clearance diameter and flow velocity (q = 5.2 mL/min)

Pressure drop ΔP [MPa]	Clearance, d [μm]	Mean flow velocity, $\overline{V}$ [m/s]
1	64.2	26.7
3	48.6	46.3
35	26.4	158.1

4. Prediction of Re-dispersed Particle Size

To predict the re-dispersed particle size, we then consider the following two forces applied to flocculated particles in the valve: shear force and van der Waals attractive force. The shear stress reduces the diameter of flocculated particles, and the van der Waals attractive force prevents the re-dispersion.

First, as the applied stress at the clearance, the shear force based on the shear stress in the back pressure valve was evaluated quantitatively. The shear stress τ [N/m^2] is expressed using the flow velocity at the clearance V [m/s] and the coordinate of radial direction y [m] as

$$\tau = -\mu \frac{\mathrm{d}V}{\mathrm{d}y} \tag{1}$$

Here, μ is the viscosity of the nanoparticle solution [kg/(m·s)]. The shear force F_{shear} [N] is then obtained by multiplying it with the cross-sectional area of the particle S [m^2].

$$F_{\mathrm{shear}} = \mu \frac{\mathrm{d}V}{\mathrm{d}y} S = \mu \frac{\mathrm{d}V}{\mathrm{d}y} \frac{\pi l^2}{4} \tag{2}$$

where l is the particle diameter. By integrating the shear force over y from the center of clearance to the wall, we obtain the mean shear force in the cross section of clearance $\overline{F}_{\mathrm{shear}}$, which is used hereafter as the shear force. By assuming the linear velocity profile, $\overline{F}_{\mathrm{shear}}$ is approximately written as

$$\overline{F}_{\mathrm{shear}} = \mu \frac{4\overline{V}}{d} \frac{\pi l^2}{4} = \mu \frac{\pi l^2 \overline{V}}{d} \tag{3}$$

To obtain the shear force, we also need to determine the mean flow velocity at the clearance $\overline{V}$ [m/s] and the diameter of clearance d [m]. From the values of pressure drop ΔP [Pa] (equal to the primary pressure) and volumetric flow rate q [m^3/s], d was calculated with assuming the equation of orifice flow [8], given as

$$q = C_0 (\pi \times d^2 / 4) \sqrt{2\Delta P / \rho_{\mathrm{S}}} \tag{4}$$

Here, C_0 is the flow coefficient (0.597), and ρ_{S} is the density of the solution (998 kg/m^3). The clearance d decreases with increasing pressure drop in the valve ΔP [Pa]. In addition, $\overline{V}$ was calculated from the estimated clearance diameter and the volumetric flow rate. The obtained diameter and velocity are summarized in Table 2.

Next, the van der Waals attractive force was calculated. The van der Waals interaction force F_{v} [J/m] is approximately expressed by

$$F_{\mathrm{v}} = \frac{Al}{24z^2} \tag{5}$$

Here, A is the Hamaker coefficient (5.74×10^{-20} kg·m^2/s^2, the value assumed to be ZnS) [9], l is the particle diameter [m], and z is the distance between the surfaces (2 nm). This is from the double surface modified captopril's diameter [10].

Fig. 3 shows the calculated forces as a function of particle diameter. For large particles, the dominant force is shear. However, the van der Waals attractive force increases with reducing particle diameter, and this force is dominant for small particles. For example, when the primary pressure is 35 MPa, the stress of van der Waals interaction energy balances with the shear stress at d = 36 nm (circled in red in Fig. 3). Table 3 shows the particle diameter that balances the shear force with the van der Waals attractive force and the mean diameter of dispersed particle obtained by the experiments. The mean diameter was comparable with that balancing the two forces. Thus, the following dimensionless numbers that represent the balance of forces (named the dispersion number, Di) approximately determines the dispersed particle diameter.

$$Di = \overline{F}_{\mathrm{shear}} / F_{\mathrm{v}} = \mu \frac{\pi l^2 \overline{V}}{d} \bigg/ \left(\frac{Al}{24z^2} \right) \tag{6}$$

The number denotes the ratio of the shear force to the van der Waals attractive force. We consider that when the two forces are balanced (in other words, the dispersion number is equal to 1), the reduction in the diameter of flocculated particles stops.

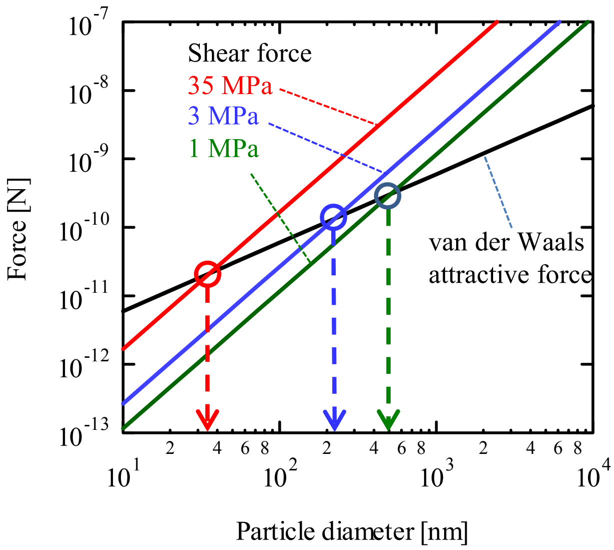

Fig. 3 Comparison of van der Waals attractive force (black) and shear forces for the three pressure drops (color).

Table 3 Particle diameter that balances the shear force with van der Waals attractive force and the mean diameter of dispersed particle obtained by the experiments

	Force balancing diameter [nm]	Experimental mean diameter [nm]
1 MPa	510	98.3
3 MPa	220	82.7
35 MPa	36	44.3

Fig. 4 shows the relationship between the estimated re-dispersed particle size that balances the forces applied to the flocculated particles and the experimental values for various conventional methods for the re-dispersion [11,12]. From the balance of forces, we can approximately predict the re-dispersed particle size. Moreover, the re-dispersion using the back pressure valve is effective to reduce the particle size less than 100 nm.

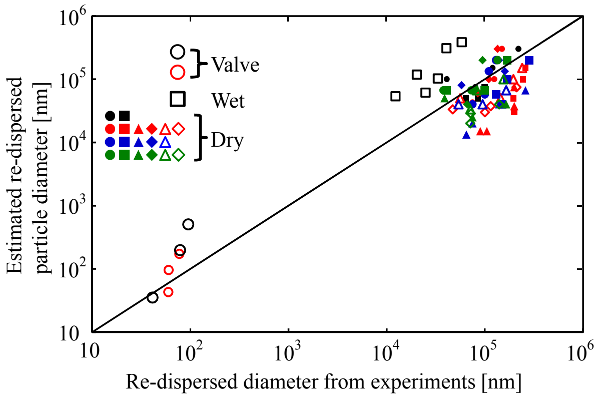

Fig. 4 Estimation of re-dispersed particle size for proposed (Valve) and conventional methods (Wet and Dry).

5. Conclusion

We have developed a new method for re-dispersing flocculated nanoparticles using a back pressure valve, in which shear stress is applied to a nanoparticle solution. In this equipment, a nanoparticle solution passes through a clearance at 158.1 m/s (35 MPa). At this clearance, a high shear is applied to the solution. Because this equipment has a small clearance, a large pressure drop occurs locally. The shear stress successfully re-dispersed the flocculated samples. Raising the pressure drop at the clearance increases the shear stress. This equipment has the potential to re-disperse not only flocculated samples, but also stronger agglomerated ones. Moreover, this valve requires no additional media such as beads. This means that the valve allows for avoiding contamination by the defacement of the media into the solution during a re-dispersion. From the balance of the shear and van der Waals forces applied to the flocculated particles, we can approximately predict the particle diameter after the re-dispersion. With this relation, we can design the operating condition of the back pressure valve. This improvement leads to the wide applicability of this valve in medical applications and nanotechnology.

Acknowledgments

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