

Spontaneous Preparation of Monodispersed, Structural Colored, Spherical Particles by Rotational Stirring

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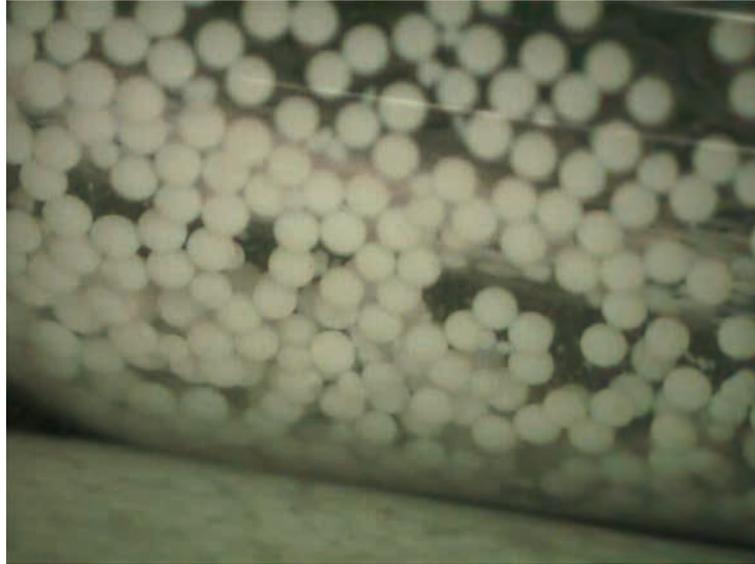
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Abstract:

When rotation stirring was applied to an electrically neutral aqueous suspension containing negatively charged, monodispersed silica fine particles and a positively charged polyelectrolyte, monodispersed, spherical particles with a size of several hundred micrometers were obtained. Conditions such as the rotational stirring speed, solute concentration, and total suspension amount were examined to clarify the conditions under which the monodispersed, spherical particles can be obtained. The spherical particles with a uniform size were obtained because the solutes create aggregates by electrostatic interactions and the flowing action of the suspension due to rotational agitation disperses the aggregates. Additionally, the obtained monodispersed, spherical particles contained monodispersed silica fine particles in submicron size aggregates with short-range order. We found that monodispersed, spherical particles with a vivid structural color can be prepared by incorporating a small amount of a black substance in the spherical particles. Because monodispersed, spherical particles with various colors can be created using silica, polymer, and carbon, which are non-toxic materials, they may be useful as new, environmentally safe pigments.



Application of rotational stirring to an electrically neutral aqueous suspension containing negatively charged monodisperse submicron-sized silica particles and positively charged polyelectrolytes gave monodisperse spherical particles of several hundred μm . In preparing this monodisperse spherical particle, it was also clarified that by adding a small amount of negatively charged black carbon black, the monodisperse spherical particle displaying vivid color can be obtained.

Combining several phenomena may result in unfamiliar, mysterious natural phenomena. One such phenomenon is the formation of round balls of ice in Lake Michigan during winter. The ice that forms on the lake surface cracks due to the wind blowing during the extremely cold winter. The cracked ice collides with other ice chunks due to the movement of waves, and round balls of ice are formed by the continual rotation. The balls of ice that reach the lake shore are unusually large with a uniform size. This occurs because water becomes ice below its freezing point, the ice is crushed by the wind and waves rotate the ice to create balls of ice that are a certain size.

Similar phenomena can also occur in the microscopic world. We discovered that spherical particles with a uniform size of several hundred micrometers can be produced by rotating and stirring an aqueous suspension of submicron-sized silica fine particles and a polyelectrolyte in a microtube (Scheme 1). Silica fine particles have a negatively charged surface and show good dispersibility in water. Polyelectrolytes dissolve by ion dissociation and are well dispersed in water. When a polyelectrolyte with a positive charge is mixed with negatively charged silica fine particles, they aggregate via ion pair formation. When amounts of a polyelectrolyte and silica fine particles are mixed to create an electrically neutral solution, a precipitate consisting of the silica fine particles and the polyelectrolyte is generated.^[1] If this suspension is placed in a microtube and rotary stirred, monodispersed, spherical particles with diameters in the range of several hundred micrometers are formed.

Generally, monodispersed particles with a submicron size or less can be prepared by using a surfactant as a stabilizer. However, larger particles are often obtained in a polydispersed state during the preparation. The larger particles obtained in the polydispersed state can be obtained as monodisperse particles by spheroidizing by some method. To obtain monodispersed particles that are larger than several tens of micrometers in a single operation, a micro-flow channel method is currently utilized.^[2] However, the micro-flow channel method is still complex. In our method, simply mixing the necessary compounds by rotation stirring produces uniform, spherical particles with a size of several hundred micrometers. The obtained particles are formed by the agglomeration of silica fine particles with a uniform particle size and short-range order and a polymer electrolyte.^[3] Therefore, because a specific wavelength of visible light is scattered and intensified in all directions, the particles are colorful and exhibit a structural color without an angle dependency.^[1c, 4]

First, the conditions under which monodispersed particles are formed from silica fine particles and a polymer electrolyte will be described. The polymer electrolyte was poly(diallyldimethylammonium chloride) (PDDA), and three molecular weight ranges, i.e., 1.0×10^5 to 2.0×10^5 , 2.0×10^5 to 3.5×10^5 , and 4.0×10^5 to 5.0×10^5 , were used. A suspension was prepared with a constant amount of silica fine particles and varying amounts of PDDA, and the ζ potential of the dispersed particles in the suspension was measured. Silica fine particles with various particle sizes were used, but the results described used silica fine particles with an average particle diameter of 282 nm. When PDDA was not added, the ζ potential of the silica fine particles in water was -50.1 mV. As the PDDA concentration increased, the ζ potential increased due to the adsorption of PDDA on the silica fine particles (Fig. 1A).^[5] However, precipitation occurred when the ζ potential was around 0 mV,^[6] and the ζ potential of the dispersion in the suspension could not be measured. Furthermore, when more PDDA was added, the suspension became transparent again, and an increase in the ζ potential of the dispersion was observed as more PDDA was added. At a high PDDA concentration, the silica fine particles are covered with PDDA, and the dispersion becomes positively charged.^[7] The change in the ζ potential and formation of precipitates as a function of the PDDA concentration were the same for the different PDDA molecular weights. Interestingly, when a suspension with a ζ potential of ~ 0 mV was rotated and stirred, uniform, spherical particles with sizes between 220 μm and 330 μm were obtained after 5 hours (Fig. 1B) regardless of the molecular weight of the PDDA. The PDDA concentration range in which particles form increased as the molecular weight of PDDA increased (Fig. S2). The transparent suspension with a measurable ζ potential did not produce a precipitate even with rotation and stirring. The time required to form the monodispersed, spherical particles decreased as the molecular weight of PDDA increased (Fig. 1C). The suspension was observed with a high-speed camera at 200 x magnification while it was rotated and stirred. The observation showed that aggregates, which were too small to confirm, were generated at the beginning (Fig. 1D: 0 min). As the rotation and stirring continued, the size of the aggregates increased, and large and small aggregates in different forms were generated (Fig. 1D: 12 min). Then, the aggregates changed into a spherical state with a uniform size (Fig. 1D: 300 min). The average particle size of the spherical particles obtained under the typical experimental conditions (see the experimental section) was 312 μm , and the standard dispersion value was 3.0%, which

indicated monodispersed particles (Fig. 1E, Fig. S3). To determine the conditions under which monodispersed particles grow, the mixing ratio of the silica fine particles and PDDA was held constant, and other factors such as the agitation speed, total solute concentration, and total suspension amount were changed. The results of using silica fine particles with a particle diameter of 211 nm are also described. PDDA with a molecular weight range of 1.0×10^5 - 2.0×10^5 was used. The experimental results are from the analysis of samples obtained after 10 hours of rotational stirring.

With an agitation speed between 70 rpm and 80 rpm, the particle shape became distorted (Fig. S4). As the agitation speed further increased, the average particle size increased (Fig. 2A), and the shape became more spherical (Fig. S4). Particles did not grow at agitation speeds below 60 rpm and above 200 rpm.

The size of the particles generated as the solute concentration changed is shown in Fig. 2B. The concentration is expressed as the concentration of the silica fine particles. As the concentration of the silica fine particles increased, the average size of the particles increased. As the concentration increased, the collision frequency of the solute increased, which is related to the growth of the particles. When the concentration of the silica fine particles was 15 wt% or more, spherical particles with a uniform size were obtained (Fig. S5).

The size of the particles obtained as the suspension amount varied is shown in Fig. 2C. The average particle size of the obtained particles was 200 μm to 300 μm from 450 μL to 1350 μL . When the suspension amount was between 600 μL and 1200 μL , the particles were monodispersed and spherical, but for suspension amounts of 400 μL and 1350 μL , mixed, distorted particles with varying sizes were obtained (Fig. S6). For suspension amounts less than 400 μL and more than 1400 μL , particle formation was not observed. Particles were probably not produced due to the change in the convection of the solution caused by the rotational stirring when the solution amount was too low or too high.

In this study, monodispersed silica fine particles with average particle sizes between 201 nm and 500 nm were used. When these particles were rotated and stirred with PDDA under conditions that induce precipitation, all of the silica fine particles became spherical particles with uniform diameters. Under the same conditions, the sizes of the obtained particles were the same irrespective of the size of the silica fine particles.

Stirring methods other than rotational stirring, i.e., stirring with a stirrer or

ultrasonic irradiation, were tested, but particulate aggregates did not form for either method.

The above results indicate that the electrical agglomeration of the silica fine particles and polymer electrolyte promotes the growth of the particles, and the suspension flow caused by rotary agitation causes the aggregates to divide and form monodispersed, spherical particles. As a result, the particles grow as spherical particles with uniform particle sizes. We do not know why the size is approximately 200 μm to 300 μm . However, the method of obtaining monodispersed, spherical particles by simply mixing the necessary materials with rotational stirring gives important information to advance granulation technology, which is required for pharmaceuticals and food engineering.

Fig. 3 shows the electron micrographs of the surface (Fig. 3B) and cross section (Fig. 3C) of the particles obtained by the above method. To evaluate the aggregation state of the silica fine particles, a Fourier transform image of the electron microscopic photograph was prepared (insertion images of Fig. 3B, 3C).^[4b, 8] The ring-shaped pattern observed in the Fourier transform image indicated that the silica fine particles are arranged in a state with short-range order. Because the refractive index has short-range order, visible light in a specific wavelength region is strengthened in every direction when monodispersed particles with a submicron size aggregate in a state with short-range order, causing interference coherent scattering.^[9] However, if it is as large as the size of the particles obtained this time, non-coherent multiple scattering will occur from the interior of the aggregate.^[4b, 4d, 10] The influence of the non-coherent multiple scattering is large, and the structural color from the aggregate particles cannot be observed with the naked eye. Thus, the particles appear to be white.^[2b, 4c] If a small amount of a black substance is added to this system, the multiple incoherent scattering is suppressed, and the effect of the coherent scattering derived from the short-range order of the refractive index becomes conspicuous.^[4b, 4c, 11] Then, the angle-independent structural color can be observed (Fig. S7).

Attempts were made to introduce black substances into the aggregates composed of silica fine particles and PDDA by adding a small amount of a black substance dispersed in water to a suspension of silica fine particles and PDDA. Here, the results from using carbon black (CB) in water are shown.^[4b, 12] CB has carboxyl groups on its surface, and when CB dissociates, it has negative charges on its surface. A photograph and the

reflection spectra of the particles obtained with silica fine particles (211 nm size), PDDA (molecular weight range of 1.0×10^5 to 2.0×10^5), and different amounts of CB are shown in Fig. 4A and 4B, respectively. The obtained particles exhibited vivid structural colors with different saturations depending on the amount of CB added. A peak for the coherent scattering derived from the short-range order formed by the fine silica particles with a particle diameter of 211 nm was observed at approximately 500 nm. Regardless of the presence or absence of CB, the position of the coherent scattering peak remained the same. The scattering intensity of the entire reflection spectra largely decreased with the addition of CB, but the net peak intensity did not decrease as much. In other words, introducing CB into the particles enhances the coherent scattering, and the resultant particles exhibit vivid structural colors. When the reflection spectra were measured (Fig. 4C inset) by changing the angle between the light irradiation direction and the detection direction, the peak position shifted to a lower wavelength as the angle increased (Fig. 4C). However, under natural light, such as sunlight, in which light comes from all directions, the structural color hue observed from these particles hardly change.^[13] Thus, particles exhibiting structural colors with a minimal angle dependence were obtained, which can be useful as pigments.^[14] If the size of the silica fine particles changed, the coherent scattering peak position changed (Fig. 5A), and particles displaying various structural color hues can be prepared (Fig. 5B).

Monodispersed, spherical particles was obtained by electrically neutralizing silica particles with a uniform particle size with positively charged PDDA in water via rotational mixing. When a small amount of water-soluble CB is added to the monodispersed, spherical particles, particles was obtained with various structural colors based on the diameter of the silica fine particles. Iron oxide (Fig. S8),^[4c] black titanium oxide and other black particles^[11a, 15] can also be used to enhance the structural coloring property of the particles. The compounds obtained by simply stirring monodispersed particles provide important knowledge for the further development of granulation technologies such as a drug formulation, food-processing and ceramic engineering. Additionally, the various colorful particles may be usable as new pigments because they contain only safe materials such as silica, carbon, and polymers. Uniform microspheres with diameters around several tens and hundreds micrometers have many uses in various fields, but classical methods such as emulsion methods are not yet useful to obtain monodisperse microspheres of these sizes. We hope that this method we found

will serve as a method to provide granulated powders of various compounds.

Acknowledgements

Y. T. acknowledges the support of Grants-in-Aid for Scientific Research (No. 15H02200 and No. 22107012) from the Ministry of Education, Culture, Sports, and Science (MEXT).

Conflict interest

The authors declare no conflict of interest.

Additional information

Supplementary Information accompanies this paper at <http://www>.

Keywords: spontaneous preparation, structural colored particles, rotation stirring, granulated powder

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Figure Captions

Scheme 1. A schematic diagram of the method for preparing monodispersed particles by rotational stirring of an aqueous suspension containing monodispersed silica fine particles and PDDA

Figure 1. A) The relationship between the ζ potential of the dispersions in the suspension of silica fine particles and PDDA and the PDDA amount is shown. The SiO₂ concentration was set at 6.67 wt%, and the measurement results were obtained by changing the PDDA concentration. Three molecular weights of PDDA were used. B) The SiO₂ concentration was 6.67 wt%, and the suspensions were prepared by changing the PDDA concentration. The size of the particles obtained after rotating the suspension at 110 rpm for 10 hours was measured as a function of the PDDA concentration. Three molecular weights of PDDA were used. C) The change in the particle size formed by rotating and stirring a suspension composed of silica fine particles and PDDA at 110 rpm was measured over time. Three molecular weights of PDDA were used. All suspensions were prepared with 6.67 wt% SiO₂ and 0.0147 wt% PDDA. D) Photographs taken with a high-speed camera while rotating and stirring a suspension of 6.67 wt% SiO₂ and 0.0147 wt% PDDA. PDDA with a molecular weight range of 1.0×10^5 - 2.0×10^5 was used. E) A photograph of the particles obtained after 10 hours of rotational stirring under the conditions used in D). For all the above samples, 750 μ L of the suspensions was used.

Figure 2. A) Relationship between the particle size and the rotation speed as the rotation speed was changed for a suspension with 6.67 wt% SiO₂ and 0.0147 wt% PDDA stirred for 10 hours; 750 μ L of the suspension was used. B) Relationship between the size of the particles obtained by rotational stirring and the silica concentration in the suspension. The mixing ratio of the silica fine particles and PDDA was constant under the conditions of A), and the particles were prepared using suspensions with different total concentrations. The rotation speed was 110 rpm, and the amount of the suspension was 750 μ L. C) Relationship between the size of the particles obtained by rotational stirring and the suspension amount. A suspension of 6.67 wt% SiO₂ and 0.0147 wt% PDDA was stirred for 10 hours at a rotation speed of 110 rpm. These results are the average of the values obtained by performing the same experiment

three times.

Figure 3. A) An electron micrograph of the particles prepared under typical experimental conditions after they were cut in half; B) Electron micrograph of the surface of the particle shown in A); C) Electron micrograph of the cross section of the particle shown in A).

Figure 4. A) A photograph of the particles obtained by adding different amounts of CB to a suspension with 6.67 wt% SiO₂ and 0.0147 wt% PDDA with a molecular weight range of 1.0×10^5 - 2.0×10^5 . B) Reflectance spectra of the particles shown in A); C) Angular dependence of the reflection spectra of the particles containing 0.83 wt% CB.

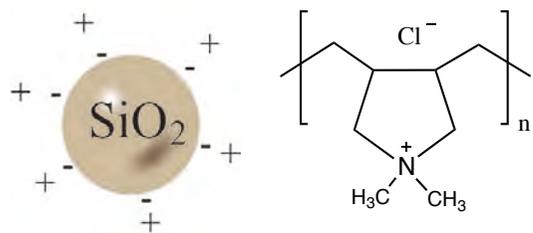
Figure 5. A), B) Reflectance spectra and photograph of the particles that formed using silica particles with various particle sizes, PDDA and CB: 0.83 wt% CB was added to a suspension of 6.67 wt% SiO₂ and 0.0147 wt% PDDA. PDDA with a molecular weight range of 1.0×10^5 - 2.0×10^5 was used.

Spontaneous Preparation of Monodispersed, Structural Colored, Spherical Particles by Rotational Stirring

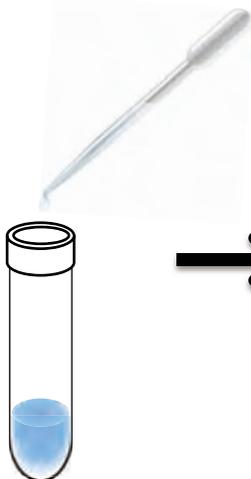
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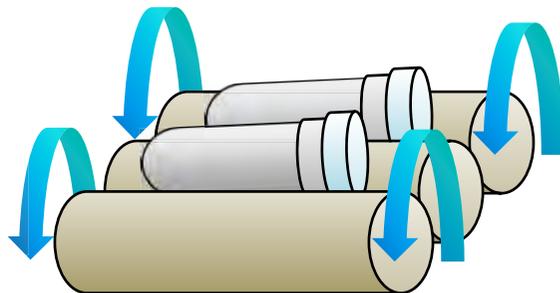
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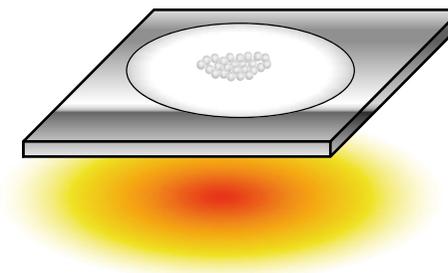
**SiO_2 particles + PDDA
in deionized water**



Rotation stirring



**Wash with
deionized water,
and dry at 80°C**



Scheme 1

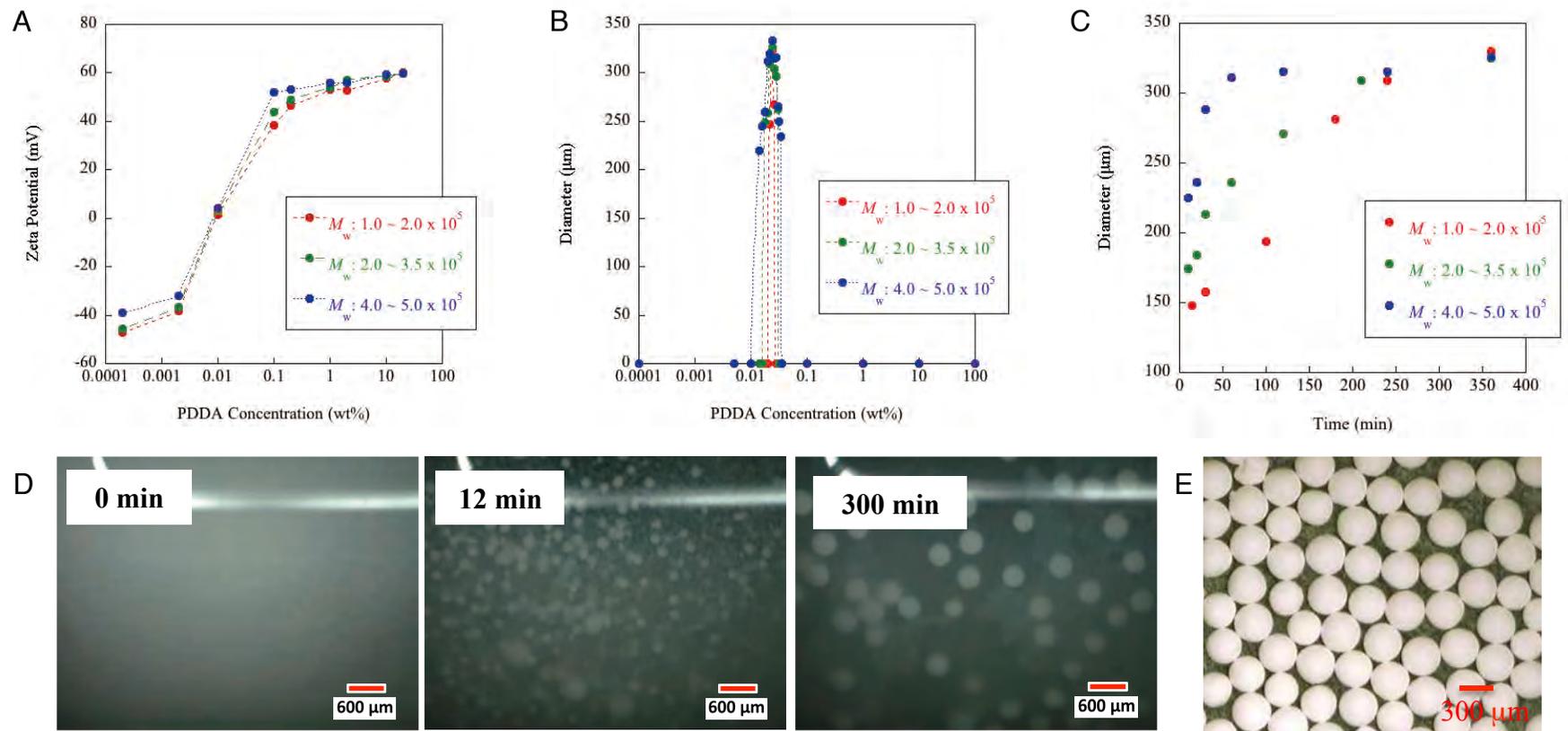


Figure 1

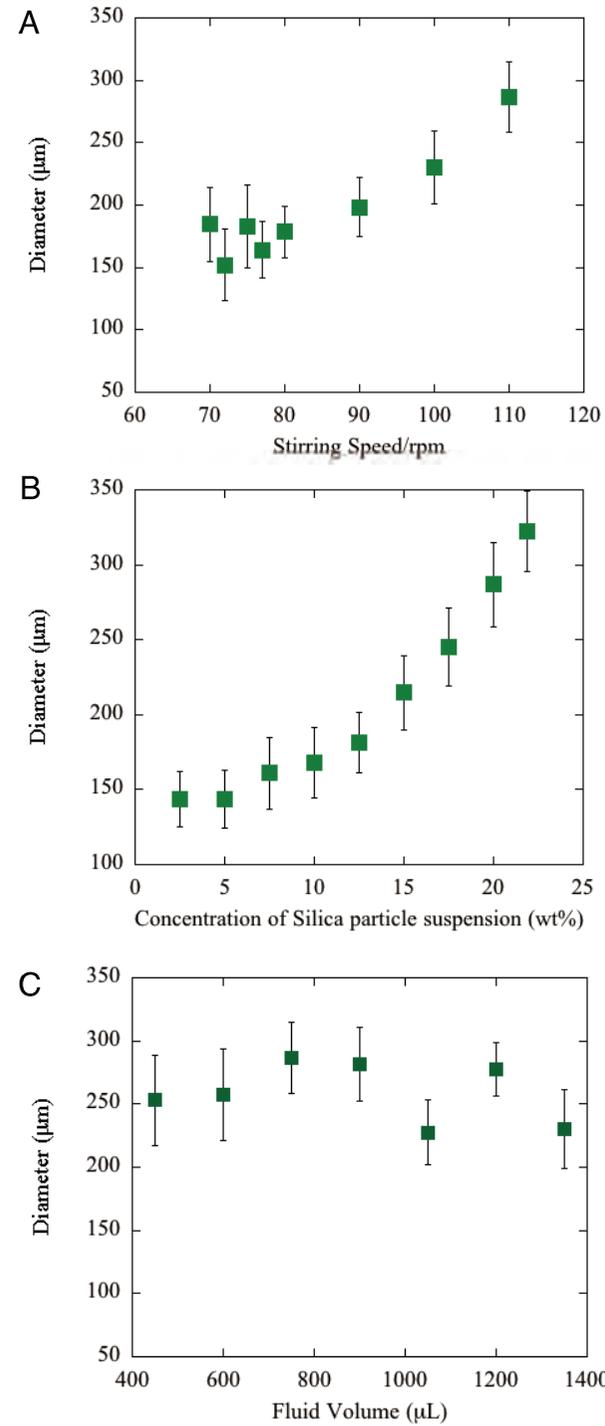


Figure 2

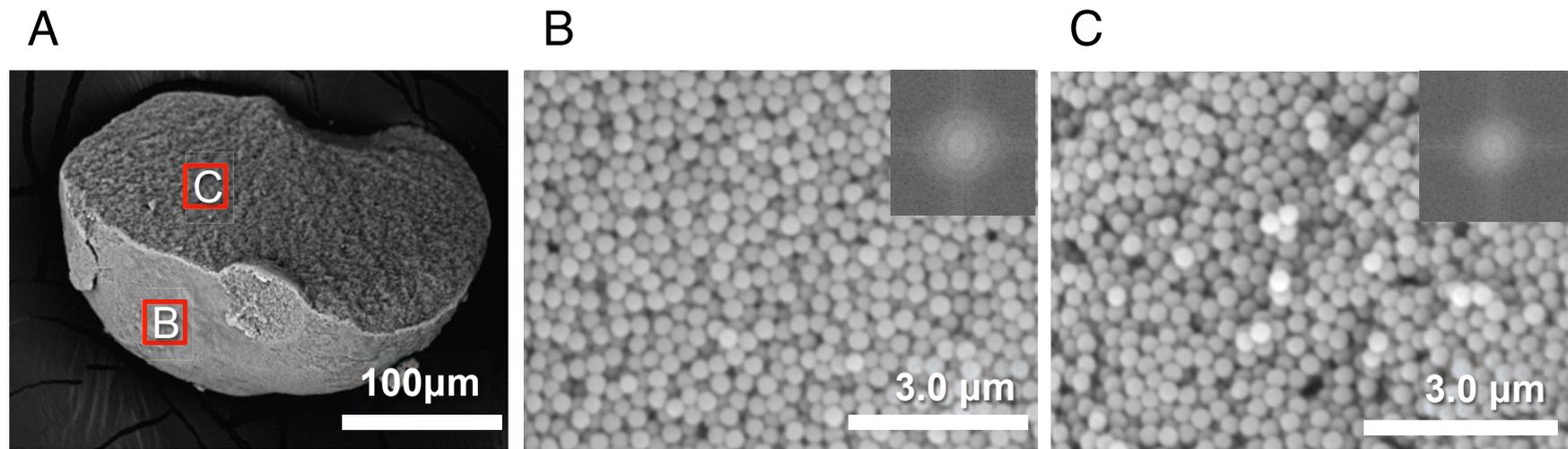


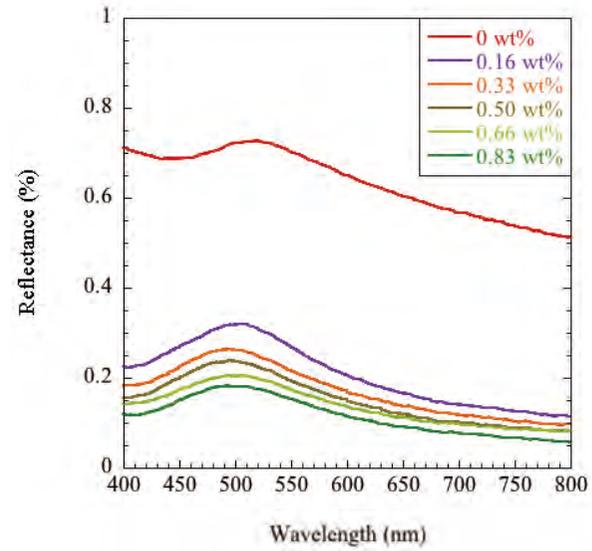
Figure 3

0 wt% 0.16 wt% 0.33 wt% 0.50 wt% 0.66 wt% 0.83 wt%

A



B



C

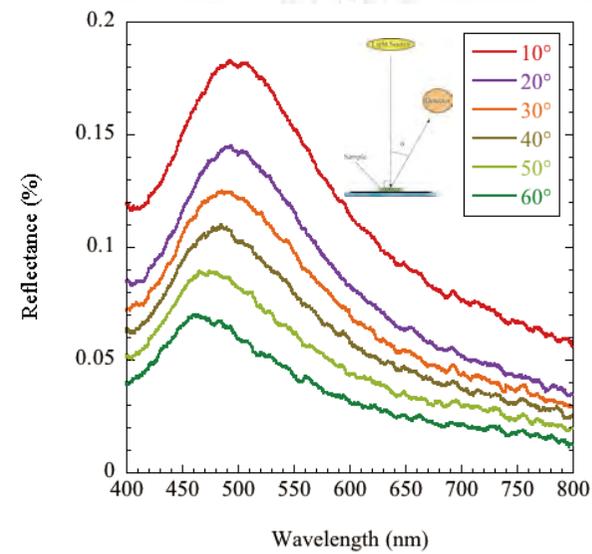


Figure 4

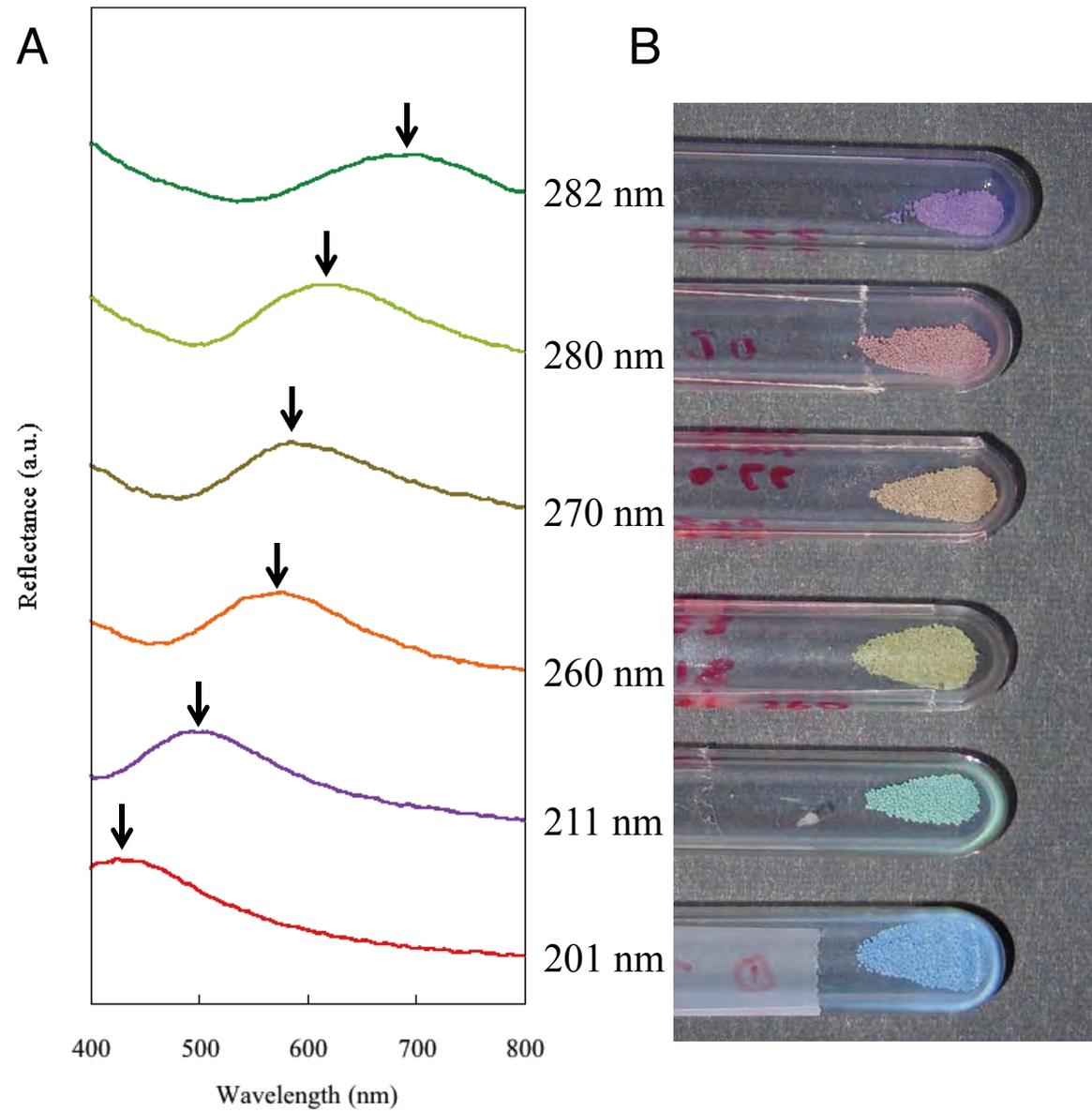


Figure 5