Self-assembly Patterning of Nano/Micro-Particles

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Abstract
We developed a self-assembly process of SiO₂ particles to fabricate desired patterns of colloidal crystals having high feature edge acuity and high regularity. A micropattern of colloidal methanol prepared on a self-assembled monolayer in hexane was used as a mold for particle patterning, and slow dissolution of methanol into hexane caused shrinkage of molds to form micropatterns of close-packed SiO₂ particle assemblies.

We further developed spherical particle assemblies and micropatterns of them. Hydrophilic regions of a patterned self-assembled monolayer were covered with methanol solution containing SiO₂ particles and immersed in decalin. Particles were assembled to form spherical shapes and consequently, micropatterns of spherical particle assemblies were successfully fabricated through self-assembly.

This result is a step toward the realization of nano/micro periodic structures for next-generation photonic devices by a self-assembly process.

Keywords: Self-assembly Patterning, Self-assembly, Colloidal Crystal, Photonic Crystal, Self-assembled Monolayer

1. Introduction
“Self-assembly” has been attracting much attention as the next generation nano/micro fabrication process. Modification of solid surface such as particles, substrates and fibers with self-assembled monolayer having desired functional groups has been developed using self-assembly. Colloidal crystals were fabricated by self-assembly of nano/micro particles to form closed pack structure such as fcc(face-centered cubic) or hcp(hexagonal closed packing). Organization proceeds with low energy consumption by the use of various interactions in the self-assembly processes. For instance, hydrophobic interaction works between OTS (octadecyltrichlorosilane) molecules, and chemical bonds are formed between “molecule and substrate” and “molecule and molecules” in the formation of self-assembled monolayers. Stabilization of energy caused from formation of these bonds ($\Delta G < 0$) is larger than decrease of entropy caused from assembly of molecules which are dispersed. These balance results in $\Delta G < 0$, therefore, molecular layer is formed by the self-assembly mechanism. Formation of molecular layer is seemingly against the second law of thermodynamics, however, it proceeds spontaneously due to the stabilization of the system caused from chemical bonds formation.

$$\Delta G = \Delta H - T \Delta S,$$  \hspace{1cm} (1)

G: Gibbs energy, H: enthalpy, T: temperature

Additionally, formation of close packed colloidal crystal by the precipitation of particles in the solution proceeds by the effect in which particles precipitate to minimize total potential energy of every particle.
Moreover, there are a great deal of self-assembly phenomena in nature, for instance, crystallization of solids in supersaturated solution, crystals of snow having various morphologies, patterns of butterflies, zebra, giraffe, and beat of the heart.

In the particle science, novel nano/micro fabrication has been developed by the use of “self-assembly”. Opal is constructed of close packed particle assembly to form fcc (hcp). Periodic architecture is formed by the combination of particles and air to be photonic crystal. Photonic crystal has photonic band gap and diffracts visible light to show structural color. There are many photonic crystals in nature, for instance, opal, morpho butterfly, blue damselfish, chrysochroa fulgidissima (schonherr), peacock etc. In order to apply photonic crystal for next generation device, patterning process of photonic crystal is required to fabricate photonic devices. In this study, we developed patterning process of colloidal crystals by the use of self-assembly. Two-dimensional patterns of colloidal crystals, spherical particle assemblies and their micropatterns were fabricated from the colloidal solution.

2. Particle Assembly for Photonic Crystal

Nano/micro periodic structures have attracted much attention as next-generation devices\(^1\) such as photonic crystals\(^2\) in which the refractive index changes periodically to show a photonic band gap. Various scientific and engineering applications, such as control of spontaneous emission, zero-threshold lasing, sharp bending of light, and so on, are expected to be become possible by using the photonic band gap and the artificially introduced defect states and/or light-emitters. The structures were prepared by semiconductor nanofabrication techniques such as lithography and etching processes\(^6, 7\), advanced wafer-fusion technique\(^8\), lithographic layer-by-layer approach\(^9\), holographic lithography\(^10\), advanced silicon microelectromechanical systems\(^11\), glancing angle deposition\(^12\) or auto cloning technique\(^13\), and theoretical studies were performed to estimate the properties of the structures. These studies confirmed the high potential of nano/micro periodic structures as future devices.

However, a simple process which requires a short time for fabrication, low energy and less amount of material needs to be developed to enable mass production. Additionally, the processes of patterning the structures need to integrate various elements for application to commercial devices. The regularity and feature edge acuity of periodic structures should also be improved in order to enhance the performance.

Nano/micro periodic structures can be prepared with short fabrication time and low energy by self-assembly of mono-dispersed particles in which particles and air (wall and air for inverse opal) are arranged periodically\(^14, 15\). Self-assembly and patterning of nano/micro particles have attracted much attention recently\(^1, 2, 16, 17\). Micropatterns of close-packed particle assemblies with high arrangement accuracy have been realized by using templates such as micromolds\(^18\), grooves\(^19\), cylindrical holes\(^20\) or trenches\(^20\). However, substrates having micromolds or grooves are necessary in these processes, and feature edge acuity and regularity need to be improved further in order to fabricate various complicated structures for photonic devices.

We have developed several patterning methods, without the use of a template, having microstructures such as molds or grooves in static solution systems\(^21\) or in drying processes\(^24, 25\) to apply them for photonic crystals. Microstructures constructed from particles such as micropatterns of particle layers, narrow particle wires, array of particle wires and so on were prepared under moderate conditions using self-assembled monolayers (SAMs). Chemical reactions and/or electrostatic interactions between particles, substrates and solutions can be easily utilized and experiments can be conducted under well-controlled conditions in the static solution system because of its static reactions. On the other hand, meniscus force and capillary force can be easily utilized for assembling particles into a close-packed structure in the drying process. However, interactions between particles, substrate and solution are difficult to use effectively and the patterning conditions are hard to control precisely because of its dynamic system so that exact nano/micro patterns are difficult to fabricate. Each patterning system has its own advantages and disadvantages. These self-assembly solution processes do not need preprocessing of micromolds or grooves. However, further progress based on novel concepts is strongly required.

Here, we developed a novel process to realize micropatterning of particle assemblies using droplets of colloidal solution and a patterned SAM. This two-solution process was developed to have the advantages of both the static solution process and the drying process. Interfacing between two solutions and shrinkage of droplets were utilized to obtain meniscus force to form densely packed particle assemblies, and ad-
ditions, the static solution system allowed precise control of the conditions. Furthermore, we proposed a novel concept for future photonic crystals. Photonic crystals in which the refractive index changes periodically have been usually prepared by the assembling of primary particles. However, spherical particle assemblies were prepared from primary particles, and periodically structure was fabricated by the orderly array of the spherical particle assemblies with our method. Spherical particle assemblies have photonic band gap derived from size, periodicity, refractive index, etc. of primary particles, and the large periodic structure fabricated from spherical particle assemblies have photonic band gap derived from size, periodicity, refractive index, etc. of spherical particle assemblies. Our newly developed method will be an initial shot for multi band gap photonic crystals.

3. SAM Preparation

An Si wafer (p-type Si [100], NK Platz Co., Ltd.) was sonicated in water, ethanol or acetone for 10 min, respectively, and exposed for 2 h to UV light (184.9 nm) (low-pressure mercury lamp, NL-UV253, Nippon Laser & Electronics Lab.) to clean the surface. The OTS-SAM or HFDTS-SAM were prepared by immersing the Si substrate in an anhydrous toluene (Acros Organics) or HFDTS (Lancaster synthesis Ltd.) for 5 min under an N\textsubscript{2} atmosphere (Fig. 1). The substrate with the SAM was baked at 120°C for 5 min to remove residual solvent and promote chemisorption of the SAM.

SAMs on the silicon substrate were exposed for 2 h to UV light through a photomask to be used as a template for micropatterning of spherical particle assemblies. UV-irradiated regions became hydrophilic due to silanol group formation, while the non-irradiated part remained unchanged. Formation of the SAMs and the modification to silanol groups by UV irradiation were verified using the water drop contact angle (θ\textsubscript{w}). The initially deposited OTS-SAM or HFDTS-SAM showed a water contact angle of 105° or 112°, but the UV-irradiated surface of SAM was wetted completely (contact angle < 5°).

4. 2D Patterning of colloidal photonic crystals

4.1 Preparation of 2D pattern of colloidal photonic crystals

SiO\textsubscript{2} particles (1 μm in diameter) (0.002 – 0.2 mg) were thoroughly dispersed in methanol (20 μl) and dropped on a patterned OTS-SAM (Fig. 1). The solution was lightly repelled by hydrophobic regions and mainly exists on hydrophilic silanol regions. The substrate was then immersed into hexane and carefully swung to remove the residual solution. The solution was repelled well by octadecyl regions in hexane. The contact angle of the methanol solution on OTS-SAM was confirmed to increase from 51.6° in air to 129.5° in hexane (Fig. 1), indicating that the methanol solution tends to exist on silanol regions selectively. Methanol was then gradually dissolved into hexane to shrink the colloidal solution mold containing particles. The shrinkage of the mold increased the concentration of particles in the solution. The particles then attracted each other by meniscus force to form a close-packed fcc (face-centered cubic) or hcp (hexagonal closest packing) structure during the drying process of methanol. Close-packed structures were thus formed on hydrophilic silanol regions selectively (Fig. 2, A to H).

4.2 Structure evaluation

2D micropatterns of multi particle-layers (Fig. 2, A and B), partially double particle-layers (Fig. 2, C and D), or single particle-layers (Fig. 2, E to H) were successfully fabricated by changing the particle concentration in the solution and solution volume per unit of hydrophilic area (SiO\textsubscript{2}/methanol 0.2 mg/20 μl for Fig. 2, A and B, 0.02 mg/20 μl for Fig. 2, C and D, 0.002 mg/20 μl for Fig. 2, E to H). 2D patterns of colloidal crystals with high regularity
The feature edge acuity of patterns and regularity in particle assembly have not been prepared by our processes previously reported\cite{21-25}. The feature edge acuity of patterns and regularity in particle assembly\cite{21-25} presented here are clearly higher than those previously reported\cite{21-25}. Fig. 2B shows a magnified area of the patterns constructed from thick particle-layers (Fig. 2A). The edge of patterns (Fig. 2, A to H) shows high feature edge acuity due to close-packing induced by meniscus force in the drying process. The core area of the particle circle (Fig. 2D, Fig. 3) was a double particle-layer of close-packed hexagonal lattice, i.e., the arrangement of fcc\{111\}, and the outer shell of the circle was a single particle-layer of hexagonal lattice (fcc\{111\}). The boundary area of these two flat terraces, i.e., inner shell, was constructed from a nested structure of square lattice, i.e., the arrangement of fcc\{100\}, to form a gentle slope between the core double-layer and outer shell single-layer. The lattice constant of the square lattice at the inner shell increased gradually with distance from the core of the circle to form a gentle slope. The difference in height was caused by the assembling process and the shape of the liquid mold in which the center is higher than the outside. The particle arrangement in the patterns constructed from a single particle-layer (Fig. 2, E to H) were assigned to the arrangement in fcc\{111\} which is a close-packed structure. The border line of particle layer in Fig. 2E showed different shape with that in Fig. 2F, G because the border line of particle layer in Fig. 2F,
G was fcc <110> and that in Fig. 2E was fcc <1/2, 1/2, 1>, which is orthogonal to fcc <1, 1, 0>. There were far fewer defects in the particle patterns than in our former processes (21-25) because of the effective meniscus force. The standard deviation for the edge of the pattern constructed from a single particle-layer (Fig. 2F) was calculated in the same manner as we reported previously (24). The center position \((x_i, y_i) \mu m\) of each particle at the edge was plotted to estimate the standard deviation. The particle at the far left in the edge line of Fig. 2F was set to be the origin of the x-y coordinate.

The approximated straight line \(f(x)\) and its slope \(\theta\) are represented as follows.

\[
f(x) = 0.0273x - 0.09, \quad (1)
\]

\[
\cos \theta = 0.996, \quad (2)
\]

The standard deviation from the approximated straight line is given by the expression,

\[
S \text{ (standard deviation)} = \sqrt{\sum_{i=1}^{n} \left( \cos \theta \cdot (f(x_i) - y_i) \right)^2 / (n-1)}, \quad (3)
\]

where \(n\) is the number of particles \((n = 35)\). Unbiased variance (U) was used because the number of particles \((n)\) is smaller than universe. The accuracy of the particle arrangement in Fig. 2F was estimated to be \(S = 8.75 \times 10^{-2}\). This is lower than that of the pattern constructed from a single particle-layer prepared in the solution using chemical reactions \(S = 3.89 \times 10^{-1}\), Fig. 7 (a) in ref. 5 (Masuda, Y.; Itoh, M.; Yonezawa, T.; Koumoto, K. Langmuir 2002, 18, 4155-4159). The standard deviation for the edge of the pattern constructed from a single particle-layer (Fig. 2H) was calculated in the same manner. Distance \((r)\) from center of a circle \((x_o, y_o) \mu m\) to each particle \((x_i, y_i) \mu m\) at the edge and its average \((\bar{r})\) are presented as follows.

\[
r_i = \left( (x_i - x_o)^2 + (y_i - y_o)^2 \right)^{1/2}, \quad (4)
\]

\[
\bar{r} = \frac{1}{n} \sum_{i=1}^{n} \left( (x_i - x_o)^2 + (y_i - y_o)^2 \right)^{1/2}, \quad (5)
\]

where \(x_o = 21.9 \mu m, y_o = 17.7 \mu m, \bar{r} = 16.53 \mu m\).

The standard deviation from the approximated circle is given by the expression,

\[
S = \sqrt{\frac{\sum_{i=1}^{n} \left( (x_i - x_o)^2 + (y_i - y_o)^2 \right)^{1/2} - r_i^2}{n-1}}^{1/2}, \quad (6)
\]

where \(n\) is the number of particles \((n = 112)\). Variance (V) was used instead of unbiased variance because the number of particles \((n)\) is the same as universe, i.e., all particles at the edge. The accuracy of the particle arrangement in Fig. 2H was estimated to be \(S = 3.89 \times 10^{-1}\). This is higher than that in Fig. 2F because a perfect circle can’t be constructed from a small number of particles which were packed in hexagonal arrangement.
Assembly process

The assembly process can be assumed from the details of structures and defects. Particle circles (Fig. 2, D and H) showed no defects at their core, implying that particles were probably assembled from the core of the particle circle and not from the outer shell. The particle circle (Fig. 2D, Fig. 3) would be formed not layer-by-layer, and the upper layer at the core was also formed before the outer shell was assembled, since the first layer at the boundary area was not a close-packed assembly. A close-packed hexagonal lattice would be formed in the lower layer as shown in the single particle circle (Fig. 2H) in the case particles were assembled layer-by-layer. Other particle patterns (Fig. 2, A to C) would be assembled from the core area in the same manner.

5. Self-Assembly Into Spherical Particle Assembly and Their Micropatterning

5.1 Self-assembly into spherical particle assembly

SiO₂ particles (1.13 μm φ, Hipresica UF N3N, CV: 3.57%, specific gravity: 1.8 ± 0.1g/cm³, Ube-Nitto Kasei Co., Ltd.) (0.2mg, 1.5 × 10¹⁰ particles) were thoroughly dispersed in water (20 μl) and dropped on a hydrophobic OTS(octadecyltrichlorosilane)-SAM. (Fig. 4). The OTS-SAM with droplets was then immersed in hexane (20 ml, solubility of hexane in water at 20°C: 0.0013g/100ml, specific gravity: 0.7) and ultrasonicated for 1 min. Large water droplets containing SiO₂ particles were separated into many small emulsions that kept them spherical on hydrophobic OTS-SAM. Water in the emulsions was gradually extracted to hexane to reduce the size of emulsions forming spherical particle assemblies. After having been immersed for 12 h, spherical particle assemblies with different diameters were observed on OTS-SAM; it was also observed that the assemblies were constructed from various numbers of particles such as 3, 5, 6, 8 or many particles (Fig. 4). Quantities of 3, 5, 6 or 8 particles were assembled into triangular, pyramidal, octahedral or decahedral particle clusters, respectively. The number of particles in spheres can be controlled by the change of emulsion size or particle concentration in water. The spherical shape of particle assemblies was caused by the high contact angle of water emulsion on hydrophobic OTS-SAM in hexane. Consequently, various sizes of spherical particle assemblies can be prepared using this emulsion process.

Fig. 4 Conceptual process for fabrication of spherical particle assemblies (first step). SEM micrographs of spherical particle assemblies with different diameters. Second left: Particle assemblies constructed from a small number of particles such as 3, 5, 6, 8 and so on. Third left: Spherical particle assembly and tilted images. Right: A large spherical particle assembly.
5.2 Formation process of small clusters of particles

The particles would be strongly bound to the droplet interfaces by surface tension in emulsions\(^{28}\). In the formation process of small clusters of particles (Fig. 4), the water in emulsions dissolved into hexane to reduce droplet size and this restricted the area in which particles could exist\(^{27}\). Particles touched together by the reduction of emulsion size and formed a spherically packed assembly. Deformation of the interface then led to the rearrangement that formed close-packed particle assemblies. The clusters were formed using emulsions not dispersed in the solution but adsorbed on the flat substrate, and thus some of the clusters showed imperfect symmetry such as pyramidal, octahedral or decahedral, which have a large flat face touching the substrate.

5.3 Linear disclinations on spherical particle assemblies

Additionally, large spherical particle assemblies (for instance \(\sim 57 \mu m\) in Fig. 4 (Right), Fig. 5) were prepared from large methanol emulsions (\(\sim 100 - 300 \mu m\)) in decalin (decahydronaphthalene) without the use of ultrasonication, which makes emulsions smaller. Many linear disclinations, i.e., grain boundaries, were formed on the surface to reduce elastic strain energy because a close-packed triangular particle lattice composed of a particle surrounded by 6 particles in plane cannot cover a spherical surface\(^{29}\). Linear disclinations were composed of an alternative arrangement of the particle surrounded by 5 particles in plane (red, this particle can be assumed to have a charge of +1) and the particle surrounded by 7 particles in plane (yellow, charge – 1). Both ends of a linear disclination were particles surrounded by 5 particles in plane to make the total charge of each linear disclination +1 as observed in\(^{29}\). The minimum number of linear disclinations can be calculated for the large sphere (\(\sim 57 \mu m\)) (Fig. 5) to be 22 (\(N\): minimum number of linear disclinations
\[N = 12 + 0.41r/d, \quad r : \text{radius of sphere } \sim 28.5 \mu m, \quad d : \text{mean particle spacing } 1.13 \mu m\)) from geometric calculations\(^{29,30}\). The surface area in a purple circle can be also calculated to be about 10.5 % of the total surface area of the sphere from the formula (chapter 5-5) (surface area ratio: \(S_2/S_1\), surface area of the sphere: \(S_1 = 4\pi r^2\), surface area in a purple circle: \(S_2 = 2\pi(r - r_1)\), radius of the purple circle shown in Fig. 5 \(\sqrt{r^2 - r_1^2} = 17.5 \mu m\)). The minimum number of linear disclinations on the surface area in a circle can therefore be estimated to about 2.3 (\(n\): minimum number of linear disclinations in a purple circle \(n = N \cdot S_2/S_1\)). However, many linear disclinations were observed in an SEM micrograph (Fig. 5). It is suggested that our assembly method can be further
optimized to reduce linear disclinations.

Furthermore, the upper sides of spherical particle assemblies were removed using a manipulator installed in an optical microscope (BX51WI Microscope, Olympus Optical Co., Ltd.) to evaluate the packing structure. Particle assemblies have a densely packed structure (Fig. 6). Particles would be completely rearranged to form a densely packed structure during the reduction of emulsion size due to the high dispersibility of particles in emulsions.

5.4 Micropatterning of spherical particle assemblies

SiO₂ particles (1.13 μm, 1 g/l) were thoroughly dispersed in methanol solution (10 μl) and dropped onto a patterned HFDTS(heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane)-SAM having hydrophobic HFDTS-SAM regions and hydrophilic silanol regions, photopatterned using a mesh for transmission electron microscopy as a photomask (Fig. 7). The patterned SAM covered with the solution was then carefully immersed in decalin so as not to remove the solution because the density of methanol (0.79) is lower than that of decalin (0.88) causing methanol to float on decalin. The patterned SAM was then gently vibrated to remove additional methanol solution and assist the movement of droplets to silanol regions. The methanol solution was selectively contacted on hydrophilic regions to form a micropattern of the solution, which became clearer after immersion for a few hours. The methanol solution containing particles formed a spherical shape because of the surface interaction between methanol, decalin and surface of a SAM and the buoyant force of methanol in decalin. Methanol in emulsions was gradually dissolved into exterior decalin phase to form

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**Fig. 6** SEM micrographs showing the inside of spherical particle assemblies formed from methanol emulsions in decalin.

**Fig. 7** Conceptual process and SEM micrographs of micropattern of spherical particle assemblies. Top left: Micropattern of spherical particle assemblies. Bottom left: Magnified area of top left. Top right: Tilted micropattern of spherical particle assemblies. Bottom right: Magnified area of top right.
particle assemblies. After having been immersed for 12 h, particle assemblies having a dome shape were formed at the center of each silanol region (Fig. 7). The distance between the centers of each spherical particle assembly was same to the distance between holes of a mesh. The diameter of spherical particle assemblies was about 18 μm. It was smaller than that of hydrophilic regions (about 100 μm) due to low particle concentration in methanol and the shape of methanol droplets on a substrate. This indicates the arrangement regularity of spherical particle assemblies can be improved more by the use of the photomask having small holes to decide positions of each droplet precisely. Some extra particles, i.e., noise particles, were also deposited on hydrophobic regions. The process should be further optimized to control many factors such as volume of methanol solution on a substrate, quality of a SAM or aggregation of particles in the solution to avoid noise particles. Particle assemblies were shown to have a densely packed structure by destructive inspection using a manipulator. Consequently, the dot array of spherical particle assemblies was successfully fabricated by this self-assembly process.

5.5 Calculation of partial surface area of a sphere for the estimation of linear disclinations (Fig. 8)

\[ y = f(x) = \sqrt{r^2 - x^2} \quad \text{(Fig. 8a-1, 2)} \]
\[ a \leq x \leq b \]
\[ a = r_i \]
\[ b = r \]
\[ r = 28.5 \mu m \]
\[ f(r_i) = \sqrt{r^2 - r_i^2} = 17.5 \mu m \]
\[ r_i = \sqrt{r^2 - (r - r_i)^2} \approx 22.5 \mu m \]
\[ S(x + \Delta x) - S(x) = \frac{2\pi}{\Delta x} \left[ f(x + \Delta x) + f(x) \right] \cdot \text{chordPQ} \]
\[ \text{chordPQ} = \sqrt{(\Delta x)^2 + (\Delta y)^2} \]
\[ \frac{S(x + \Delta x) - S(x)}{\Delta x} = \pi \left[ f(x + \Delta x) + f(x) \right] \cdot \sqrt{1 + \left( \frac{\Delta y}{\Delta x} \right)^2} \]
\[ \lim_{\Delta x \to 0} \frac{S(x + \Delta x) - S(x)}{\Delta x} = S'(x) \]
\[ \lim_{\Delta x \to 0} \pi \left[ f(x + \Delta x) + f(x) \right] \cdot \sqrt{1 + \left( \frac{\Delta y}{\Delta x} \right)^2} = \pi \cdot 2 f(x) \cdot \sqrt{1 + \left( \frac{dy}{dx} \right)^2} \]
\[ \Delta x \to 0 \]
\[ S'(x) = 2\pi \cdot f(x) \cdot \sqrt{1 + \left( \frac{dy}{dx} \right)^2} \]
\[ g(x) = 2\pi \cdot f(x) \cdot \sqrt{1 + \left( \frac{dy}{dx} \right)^2} \]
\[ g'(x) = 2\pi \cdot f'(x) \cdot \sqrt{1 + \left( \frac{dy}{dx} \right)^2} \]
\[ S'(x) = g(x) \]
\[ \int_a^b g(x) \, dx = \left[ S'(x) \right]_a^b \]
\[ = S(b) - S(a) \]
\[ = S(b) - 0 \]
\[ = S \]
\[ \therefore S = \int_a^b 2\pi \cdot f(x) \cdot \sqrt{1 + \left( f'(x) \right)^2} \, dx \]
\[ f(x) = \sqrt{r^2 - x^2} \quad \text{(Fig. 8b)} \]
\[ f'(x) = \frac{1}{2} \left( -2x \right) \cdot \frac{1}{\sqrt{r^2 - x^2}} = \frac{x}{\sqrt{r^2 - x^2}} \]
\[ S = \int_0^r 2\pi \cdot \sqrt{r^2 - x^2} \cdot \sqrt{1 + \left( \frac{x}{\sqrt{r^2 - x^2}} \right)^2} \, dx \]
\[ = \int_0^r 2\pi \cdot \sqrt{r^2 - x^2} \cdot \frac{(r^2 - x^2) + x^2}{r^2 - x^2} \, dx \]
\[ = \int_0^r 2\pi \cdot r \, dx \]
\[ = 2\pi \cdot r \int_0^r dx \]
\[ = 2\pi \cdot r \left( r - a \right) \]
\[ a = r_i \]
\[ b = r \]
\[ S_2 = 2\pi r \left( r - r_i \right) \]
\[ \frac{S_2}{S_1} = \frac{2\pi r \left( r - r_i \right)}{4\pi r^2} = \frac{r - r_i}{2r} = 0.105 \]
\[ r = 28.5 \mu m \]
\[ d = 1.13 \mu m \]
\[ N = 12 + 0.41r/d \]
\[ \approx 22 \]
\[ n = N \times \frac{S_2}{S_1} \]
\[ = 22 \times 0.105 \]
\[ = 2.3 \]
6. Conclusion

We proposed a novel self-assembly process to fabricate micropatterns of particle assemblies, without the use of a template, having microstructures such as molds or grooves. 2D micropattern of colloidal crystal and a two-dimensional array of spherical particle assemblies were fabricated by self-assembly with this method. Interfacing between two solutions and shrinkage of droplets were utilized to obtain meniscus force to form particle assemblies, and additionally, its static solution system allowed precise control of the conditions. These showed the high ability of self-assembly processes to prepare microstructures constructed from colloidal crystals. Further investigations of the solution-solution, solution-SAMs and solution-particles interfaces and the behavior of particles and solutions would allow us to develop this two-solution system to prepare desirable particle assembly structures.

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Fig. 8 Calculation of partial surface area of a sphere.

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Author’s short biography

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Dr. Yoshitake Masuda is a researcher at the National Institute of Advanced Industrial Science and Technology (AIST). He graduated from Tsukuba University in 1994, and received his Master of Engineering degree from Tsukuba University in 1996. He was an engineer at NGK Spark Plug Co., Ltd., from 1996 to 1998. Dr. Masuda was an assistant professor at Nagoya University from 2000 to 2006. He received his Doctor of Engineering degree from Nagoya University in 2004. His PhD thesis was on the Patterning of TiO2 Thin Films and Particles using Self-assembled Monolayers.