

SEQUENTIAL SELF-ASSEMBLY BY CONTROLLING INTERACTIVE FORCES BETWEEN MICROPARTICLES

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ABSTRACT

This paper describes binding-sequence control in self-assembly of microparticle by changing interactive forces from the outside. We demonstrated a sequential self-assembly with two binding steps. At the 1st step, the microparticles primarily start to bind to each other on their hydrophobic surfaces (surface A) in aqueous solution. After changing the pH of the solution, the particles subsequently connect on their hydrophilic surfaces (surface B) at the 2nd step. We confirmed that this sequential process increases the yield of the assembled structure, and concluded that pH control is effective to achieve a sequential self-assembly.

1. INTRODUCTION

Self-assembly is a phenomenon in which basic units form a structure spontaneously. It is observed in nature on a small scale: crystal growth, biological membrane, micelle formation, and DNA replication. Self-assembly is quite common in the biological world; three-dimensional complex structures are often formed using interfacial interaction and shape selective recognition.

Self-assembly is now being applied to nanotechnology—a “bottom-up” scheme has been used to create new functional materials and devices. Several micro self-assembly techniques have been also proposed for micro-scale applications. Many microparts are fabricated separately and then mixed and self-assembled. This approach has the potential to create new devices and structures that cannot be fabricated with conventional technologies. Using micro self-assembly techniques, electrical/optical devices and three-dimensional structures have been fabricated [1-4]. In MEMS2003, we also proposed three-dimensional self-assembly using hydrophobic interaction [5].

However, complex structures such as “closed structure” cannot be fabricated because the bindings were achieved depending only on a design and characteristic of the binding surfaces by these techniques. Control of binding sequence, which is observed frequently in biological world, is needed to fabricate this kind of structures. In this paper, we’ve proposed a binding-sequence control method of micro self-assembly. Sequential self-assembly with two binding steps have been demonstrated. Figure 1 shows our concept. The interaction between microparticles was changed from the outside by changing the pH of the solution.

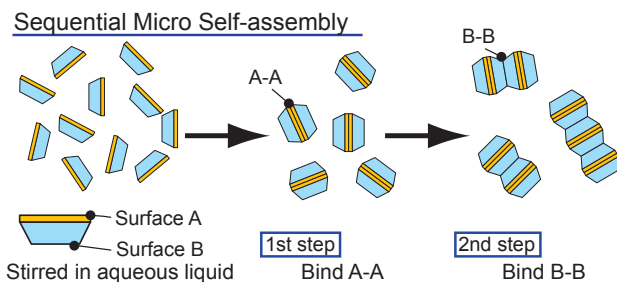


Figure 1: Concept of sequential self-assembly with two binding steps.

We’ve shown that the assembled structure was obtained with high yield by the sequential process.

2. CONTROL MECHANISM OF BINDINGS

Figure 2 illustrates a control mechanism of the bindings of the microparticles. Three interactive forces totally act between the particles in aqueous solution: hydrophobic attractive interaction, van der Waals’ attractive interaction, and electrostatic repulsive interaction. Balance of these interactions determines whether the surfaces can be bound or not.

The microparticles we fabricated have two binding surfaces: an octadecanethiol (ODT)-formed Au surface (surface A, hydrophobic) and a SiO₂ surface (surface B, hydrophilic). The hydrophobic interaction strongly acts between the surface A-A in aqueous solution. The electrostatic repulsive interaction hardly acts between A-A because the surface A has no electric charge. Therefore, the surfaces A-A were attracted to each other not depending on the pH of the solution. Though the surface B has electric charges generating electrostatic repulsive interaction when the pH is 6.5, the charges disappear when the pH is 3 (iso-electric point) because of static reaction between the surface and H⁺ ions of the solution. Therefore, though the repulsive interaction was stronger than the attractive interactions when the pH is 6.5, the attractive interactions exceed the repulsive interaction when the pH is 3. It means that the total interaction between B-B can be switched from repulsion to attraction by changing the pH.

We predicted the bindings of the particles by calculating potential energy between two surfaces. As a function of the distance, d , between two surfaces,

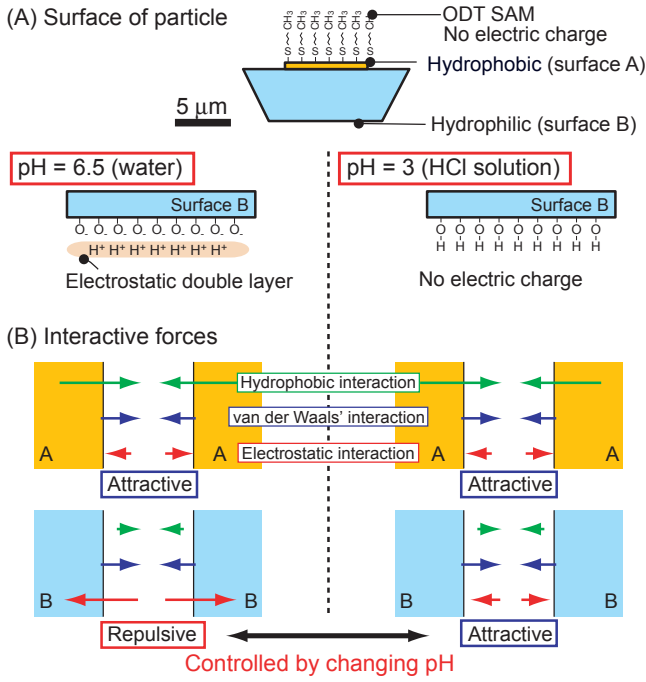


Figure 2: Control mechanism of bindings. (A) Surface characteristics of particles. The surface A, which was modified by ODT SAMs, is hydrophobic and has no electric charge in aqueous solution. The surface B, which was chemically oxidized SiO_2 , is hydrophilic and has electric charges depending on the pH of the solution. (B) Interactive forces acting between the surfaces of microparticles. Length and direction of the arrows indicate the strength and direction of these interactions.

hydrophobic interaction, V_H , Van der Waals' interaction, V_A , and electrostatic interaction, V_R , are given by,

$$V_H = -2\gamma_{\text{SL}} \exp(-d/\lambda_0), \quad (1)$$

$$V_A = -\frac{A}{48\pi d^2}, \quad (2)$$

$$V_R = \frac{0.048\sqrt{C}}{z} \gamma^2 \exp(-2\kappa d), \quad (3)$$

where

$$\gamma = \frac{\exp(ze\psi/2kT) - 1}{\exp(ze\psi/2kT) + 1}, \quad \kappa = \left(\frac{1000z^2 e^2 CN_A}{\epsilon_r \epsilon_0 kT} \right)^{\frac{1}{2}},$$

γ_{SL} is the interfacial free energy between the surface and the solution, λ_0 is the decay length ($\lambda_0 = 1$ nm), A is the Hamaker constant, C is the concentration of counter ions, z is the electrobalance, ψ is the electrical potential of the surface, ϵ_r is the relative permittivity, ϵ_0 is the permittivity in vacuum, k is the Boltzmann constant, T is the absolute temperature, e is the elementary charge, N_A is the Avogadro's constant.

Total potential energy, V_T , between the surfaces was calculated using Derjaguin-Landau-Verwey-Overbeek (DLVO)-based theory. Adding the term of V_H to the DLVO theory, V_T is given by,

$$V_T = V_A + V_H + V_R \quad [6]. \quad (4)$$

Table 1 shows the parameters for the potential energy calcul

Table 1: Parameters for potential energy calculation.

Surfaces	pH	ψ [mV]	C [mol/l]	γ_{SL} [mJ/m ²]	A [10^{-20} J]
A-A	6.5	0	$10^{-6.5}$	42.1	0.5
A-A	3	0	10^{-3}	42.1	0.5
B-B	6.5	-50	$10^{-6.5}$	0	6.0
B-B	3	0	10^{-3}	0	6.0

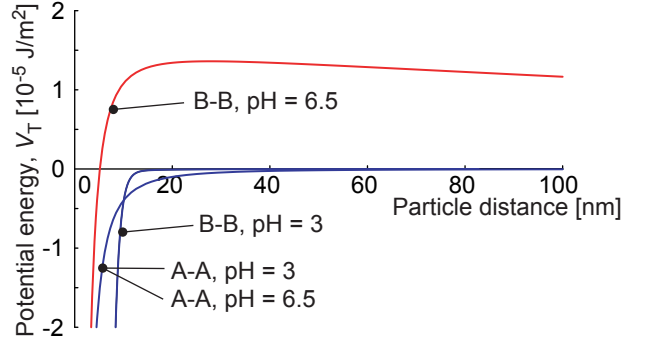


Figure 3: Potential energy calculation between the surfaces.

-ation. We calculated the γ_{SL} using the values of contact angle measurement of water, diiodomethane and ethylene glycol. We assumed that the ψ of the surface A was 0 mV because the methyl terminal group (CH_3 -) was not ionized in aqueous solution. The value of the Hamaker constant, A , of the surface A was referred to a value of hydrocarbons. As for ψ and A of the surface B (SiO_2), values of silica particle were referred. Figure 3 shows the V_T between A-A and B-B when the pH is 6.5 and 3, respectively. Potential wall only exists between B-B at the pH of 6.5. It indicates that repulsive force acts on B-B at this pH, and attractive force acts on the others.

Using this principle, the sequential self-assembly was accomplished; the particles were stirred in deionized water (pH = 6.5) and bound to each other on the surface A as the 1st step; After that, changing the pH to 3 by replacing water to 0.01 M hydrochloric acid (HCl) solution (pH = 3), the surfaces B were subsequently bound as the 2nd step.

3. BINDING-CONTROL EXPERIMENTS

Binding force measurement

The binding force between the particles is expected to change depending on the pH of the solution. We measured the binding force between a microparticle and a substrate using a micromachined piezoresistive cantilever in pH-adjusted solution. Figure 4 shows a schematic illustration and a photograph of the binding-force measurement. Controlling the cantilever with XYZ-manipulator, we measured shearing force to flick the particle. We assumed that the surface property of the substrate is equal to that of the particle. The length of the cantilever is 200 μm , the width is 30 μm , the thickness is 340 nm, the spring constant is 0.003 N/ μm , and $(\Delta R/R)/\Delta x$ is 602 $\mu\text{strain}/\mu\text{m}$. Fabrication process of the microparticles and the cantilever are given in elsewhere [5] and [7], respectively.

Table 2 shows the binding force between

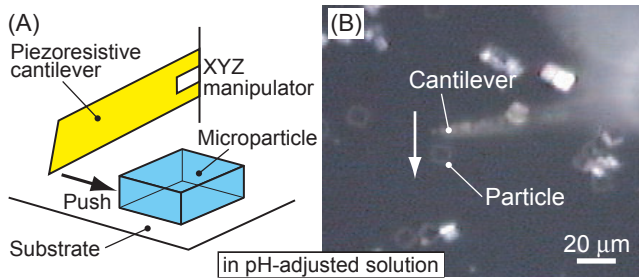


Figure 4: (A) Illustration and (B) photograph of the binding force measurement. The binding force was measured in the pH-adjusted solution.

Table 2: Binding force between microparticle and substrate measured by the cantilever. Thirty particles were measured at each condition. “~0” indicates that the binding force was too weak to be measured or the particles floated on the substrate because repulsive force acted between them. “115~” means that the binding force was too strong to flick the particle by this cantilever.

Particle	Substrate	pH of solution	
		6.5 (1st step)	3.0 (2nd step)
(A-A) ODT/Au	ODT/Au	115~* [nN]	115~* [nN]
(B-B) SiO ₂	SiO ₂	~0* [nN]	2.53 ± 1.24 [nN]

*Out of the measurement range of the cantilever.

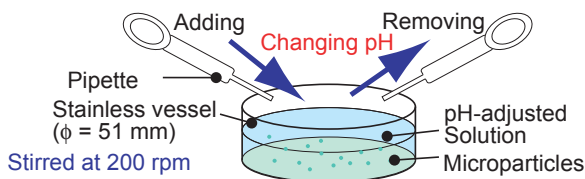


Figure 5: Illustration of the binding control experiment.

ODT/Au-ODT/Au and SiO₂-SiO₂ in water (pH = 6.5) and 0.01 M HCl (pH = 3), respectively. Two ODT/Au surfaces (A-A) were strongly bound to each other both in the pH of 6.5 and 3. The binding force between two SiO₂ surfaces (B-B) changes: nearly zero at the pH of 6.5 and 2.53 nN on the average at the pH of 3. This experimental result agreed with the prediction of the potential calculation.

Binding control experiment

Binding-control experiments were carried out to confirm the possibility of controlling the bindings between the surfaces B-B by changing pH. Figure 5 shows a schematic diagram of the experiment. A stainless vessel was filled with a pH-adjusted solution. Particles with SiO₂ surfaces (surface B) on both sides were stirred at 200 rpm with a shaker while the pH was changed by adding and removing the solution with a pipette. HCl and NaOH were used to adjust the pH of the solution. The solution was kept at the same volume. The pH of the solution started at 12, decreased to 3 by adding water and HCl, and increased again to 13 by adding water and NaOH.

Figure 6 shows that the average number of particles comprising an assembled structure in various pH of the solution. Though the particles were taken apart around the

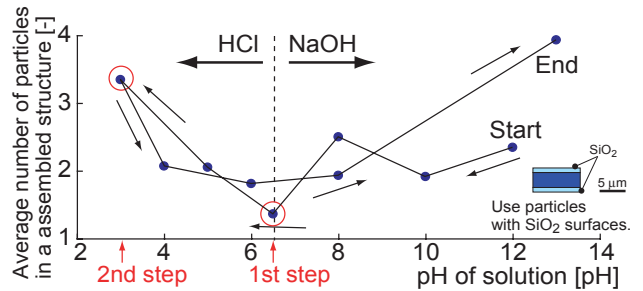


Figure 6: Changes in number of SiO₂ particles comprising an assembled structure. The pH of the solution was changed dynamically during the assembling process.

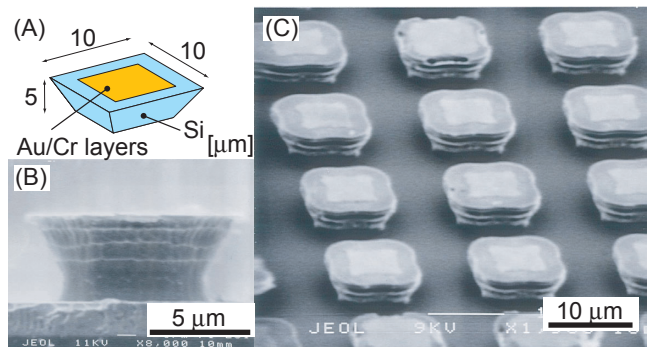


Figure 7: (A) Design of the microparticle. (B) Side-view SEM photograph of the microparticle. (C) Bird's-eye view SEM photograph of the microparticles fabricated on a wafer.

1. Evaporate Au/Cr layers on SOI wafer
2. Pattern Au/Cr layers
3. Etch Si by DRIE
4. Release particles by HF
5. Modify Si by piranha to grow SiO₂ layer
6. Modify Au by ODT SAMs

Figure 8: Fabrication and surface modification process of the microparticles.

pH of 6.5, they were assembled when the salt concentration is high such as the pH of 3 or 12. The result indicates that the bindings between the particles can be controlled by this method.

4. SEQUENTIAL SELF-ASSEMBLY

Particle fabrication

The microparticles for the sequential self-assembly were fabricated. Figure 7 shows a design and SEM photographs of the microparticles. The size of the particle was 10 x 10 x 5 μm. The Au/Cr layers were patterned on the top surface. The side walls were tapered by DRIE etching to discriminate the top and the bottom of the particle. About 1 million particles were fabricated on a diced SOI wafer (25 x 25 mm) at a time.

Figure 8 summarizes fabrication process of the

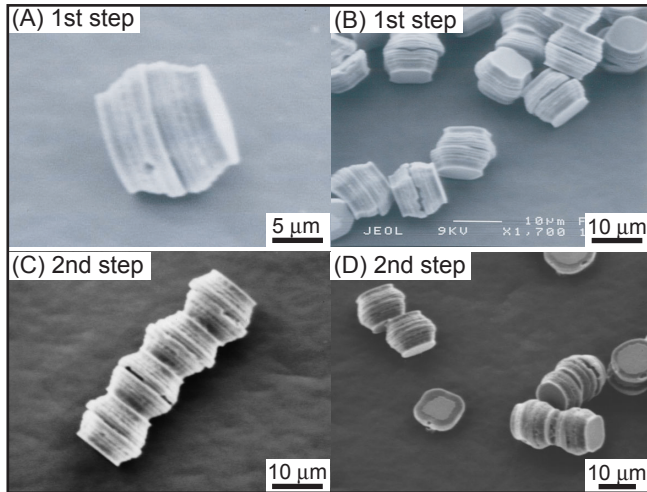


Figure 9: SEM photographs of sequentially self-assembled microparticles. (A)(B) Assembled particles after the 1st step. (C)(D) Assembled particles after the 2nd step.

Table 3: Yield comparison of the assembled structure after 2nd step. Assembly process without sequence means that the particles were stirred in solution of the pH of 3 from the beginning.

Process	Yield of the assembled structure [%]	
Without sequence (pH = 3)	8.86	
With sequence		
1st step (pH = 6.5)	0.00	(67.9)*
2nd step (pH = 3)	18.3	

*Yield of the structure shown in Figure 9(A) and (B).

microparticles. Au/Cr (50/5 nm) layers were evaporated on a diced SOI (5/2/450 μm) wafer and patterned by gold etchant (KI + I₂) and chromium etchant. Si layer was obliquely etched by DRIE to form the structure of the particles. The particles were released by HF in a microtube, deposited at the bottom of the tube with a centrifuge, and rinsed by replacing the HF to water. The Si surface of the microparticle was oxidized to SiO₂ by piranha, and the Au surface was modified by ODT SAM. The details of the process of the surface modification are given in our previous work [5].

Sequential self-assembly

The sequential self-assembly with two binding steps was carried out. We used the same experimental setup shown in Figure 5. The fabricated microparticles were stirred in water (pH = 6.5) at 200 rpm, for 3 min, at the 1st step. After that, water was replaced to 0.01 M HCl (pH = 3) and stirred for 3 min at the 2nd step. Figure 9 shows SEM photographs of the self-assembled microparticles after the 1st and 2nd steps, respectively. We can observe that the particles bound to each other on their surface A in Figure 9(A) and (B), and the sequentially assembled structure in which the particles bound on A-A and B-B.

To confirm that the structures were really assembled with sequential steps, we compared the yields of the structures fabricated with and without the sequential process.

In the case of the process without sequence, the particles were stirred in HCl solution in the first place. Table 3 shows the yield comparison of the assembled structures. The yield of the structures with sequence was 18.3 %, which was roughly twice the yield without sequence, 8.86 %. We presented that the sequential self-assembly were actually accomplished and the sequential process can increase the yield of the assembled structure.

5. CONCLUSION

We proposed the sequential self-assembly which the sequence was controlled from the outside. The sequential self-assembly with two binding steps was demonstrated by changing pH. The microparticles with two binding surfaces were fabricated and stirred in pH-adjusted solution. The interaction between the SiO₂ surfaces was switched from repulsive to attractive by changing the pH. Using this principle, we successfully accomplished the sequential self-assembly with two binding steps. We achieved the high yield of the sequentially assembled structure, 18.3 %, compared to the yield of the structure assembled without sequence, 8.86 %.

We concluded that this sequential process increases the yield of the assembled structure and that pH control is effective to achieve a sequential self-assembly.

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