

Chapter 4

Particle assembly and patterning

4.1 Introduction

Patterning and assembly of nano/micro particles have attracted great interest for applications in future devices such as photonic devices, single electron devices and so on. We have been trying to develop self-assembly processes of nano/micro particles. We used molecular recognitions and chemical reactions in the solution (chapter 4.3, 4.4, 4.5) and capillary force in drying processes (chapter 4.6, 4.7).

In chapter 4.3, site-selective deposition of particles was realized by the use of chemical reactions between particles and SAMs. Micropattern of randomly deposited particles was fabricated in the solution at room temperature.

In chapter 4.4, Micropattern of close-packed particle layer was fabricated through the formation of siloxane bonds between particles and SAMs. Furthermore, SAMs were modified by the AFM lithography technique or a mechanical modification technique with a diamond tip and micropatterns of particles were fabricated on the patterned SAMs.

In chapter 4.5, we improved our patterning method to realize precise arrangement of particles. Particles were arranged on silanol groups of SAMs to form close-packed particle wires. Each particle was put on desired position modified by AFM lithography. Furthermore, micropattern of close-packed particle layer was fabricated using electrostatic interaction between particles and SAMs.

In chapter 4.6, micropatterns of particle assembly were fabricated using a liquid mold and its drying process. Particles were assembled to have regularity in their array by capillary force in the drying process. Patterns of a close-packed particle layer and particle wires were fabricated in the solution previously (chapter 4.2, 4.3, 4.4). Severe control of many factors was necessary to realize a close-packed structure and high accuracy because capillary force cannot be used in the solution. A close-packed structure can be easily obtained in our unique process compared with our previous process. Furthermore, non-close-packed structure was realized by the control of drying process.

In chapter 4.7, an orderly array of particle wires constructed from a close-packed structure was fabricated from colloidal solution. This process doesn't require the preparation of patterned templates and movement of liquid surface was used for assembly and patterning of particles.

4.2 Experimental procedure

SAM preparation

P-type Si (100) wafers were employed for the substrates. These were cleaned ultrasonically in deionized water ($> 17.6 \text{ M}\Omega\text{cm}$), immersed in a 1:1 (vol.) HCl:CH₃OH solution for 30 min, and cleaned again in deionized water. They were further immersed in conc. H₂SO₄ for 30 min and then in boiling water for 5 min, and were cleaned with acetone. PTCS-SAM was prepared by immersing the substrate into an anhydrous toluene (99.8 %, Aldrich) solution containing 1 vol% PTCS (Aldrich) for 5 min under a N₂ atmosphere. The substrate with a PTCS-SAM was then baked at 120 °C for 5 min to remove residual solvent and to promote chemisorption of the SAM.

Surface modification of SAM by UV irradiation

PTCS-SAM was exposed for 2 h to UV light (184.9 nm) from a Hg lamp through a photomask. The UV-irradiated regions became hydrophilic due to Si-OH group formation, while the nonirradiated part remained unchanged, *i.e.*, it was composed of hydrophobic phenyl groups, which gave rise to a patterned PTCS-SAM.^{6,9} In order to check for successful film formation and functional group change, the water drop contact angle was measured for both irradiated and nonirradiated surfaces. Initially deposited PTCS-SAM showed a water contact angle of 74 °, but the UV-irradiated surface was wetted completely (contact angle $< 5^\circ$). These SAMs were used for the sphere arrangement in the presence of hydrochloric acid.

4.3 Site-selective deposition of particles to form randomly deposited particle layers using ester bonds formation

Site-selective deposition of particles was realized by the use of chemical reactions between particles and SAMs. Micropattern of randomly deposited particles was fabricated in the solution at room temperature.

Surface modification of SiO₂ spheres

Silica spheres (A : 15 nm ϕ , dispersed in a methylethylketone, Nissan Chemical Industries, Ltd., MEK-ST, B : 500 nm ϕ , powder, Admatechs Co., Ltd., SO-E2) were immersed in a dicyclohexyl and sonicated for 10 min under a N₂ atmosphere for good dispersion (Fig. 1). 1 vol% trichloroethoxysilane (TCES) was added to the dicyclohexyl solution under a N₂ atmosphere, and the solution was stirred gently for 10 min in order to chemisorb TCES onto the SiO₂ sphere surfaces (Fig. 2). SiO₂ spheres with TCES were centrifuged several times to remove unreacted TCES using dicyclohexyl. SiO₂ spheres with TECS were then baked at 120 °C for 5 min to remove residual solvent and to promote chemisorption of the TCES.

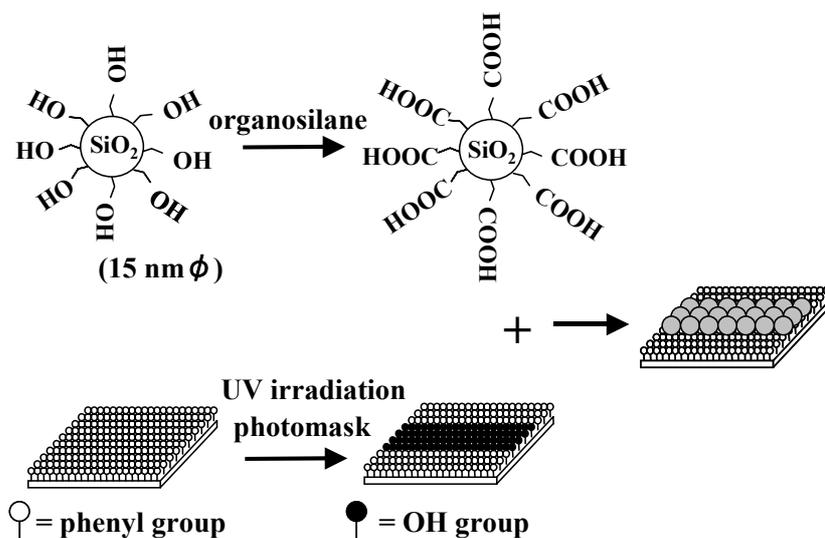
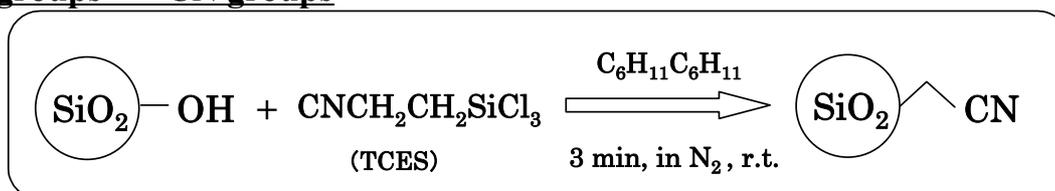


Figure 1. Conceptual process for arranging fine silica spheres on SAM.

The SiO₂ spheres with TCES were further dispersed in a tetrahydrofuran solution containing potassium tert-butoxide (t-BuOK) and 18-crown 6-ether for 24 h under an ambient atmosphere to oxidize the CN-groups to carboxyl groups.¹ This reaction was initiated by deprotonation at a C-H adjacent to the nitrile, and an oxidative cleavage transformed the carbon α to the nitrile into the carboxyl group. The solution was centrifuged to remove tetrahydrofuran, and a brown precipitate was obtained. This was further centrifuged

several times using distilled water to remove t-BuOK, 18-crown 6-ether, and a tetrahydrofuran, and a white powder was finally obtained after centrifugation. Fine SiO₂ spheres (A : 15 nm ϕ) were difficult to sediment by centrifugation because of their small size, so that HCl was added to the tetrahydrofuran solution after the oxidation reaction to control the pH of the solution to equal to an isoelectric point (pH = 1.8).² This treatment enabled us to easily sediment SiO₂ spheres.

OH groups \rightarrow CN groups



CN groups \rightarrow COOH groups

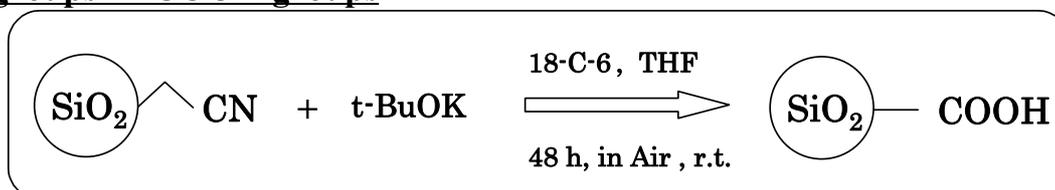


Figure 2. Conceptual process for surface modification of SiO₂ spheres.

Surface modification for the SiO₂ spheres was monitored using IR (Infra red) spectroscopy (270-30, Hitachi, Ltd.) as shown in Fig. 3. C \equiv N stretching band at 2256 cm⁻¹ is clearly observed for SiO₂ spheres (c) treated with TCES whose spectrum is shown in (a), indicating TCES is chemisorbed on the surfaces of the SiO₂ spheres (b). The absorption band at 1634 cm⁻¹ - 1700 cm⁻¹ appearing in the spectrum (d) can be assigned to a C=O stretching vibration, demonstrating that the CN groups on the sphere surfaces were successfully oxidized to carboxyl groups by the treatment with t-BuOK. In order to further examine these reactions, the SiO₂ spheres were treated in the same manner as described in the experimental section, but using no TCES. C \equiv N and C=O stretching bands were not observed in a spectrum of these SiO₂ spheres. It was thus verified that the C \equiv N and C=O stretching vibration bands originated from TCES and carboxyl groups derived from TCES by oxidation, respectively.

A Si wafer was also treated with TCES, and the oxidation of the CN groups was evaluated by x-ray photoelectron spectroscopy (XPS) (ESCALAB 210, VG Scientific Ltd.). The x-ray source (MgK α , 1253.6 eV) was operated at 15 kV and 18 mA. The pressure of the analysis chamber was 1-3 \times 10⁻⁷ Pa. The spectral peak corresponding to N 1s binding energy centered at 400.9 eV, while C 1s (285.5 eV) and O 1s (531.3 eV) were observed from the surface of TCES-treated Si substrate on which TCES-SAM was formed (Fig. 4). The intensity of N 1s peak greatly decreased after the substrate was treated with t-BuOK. The

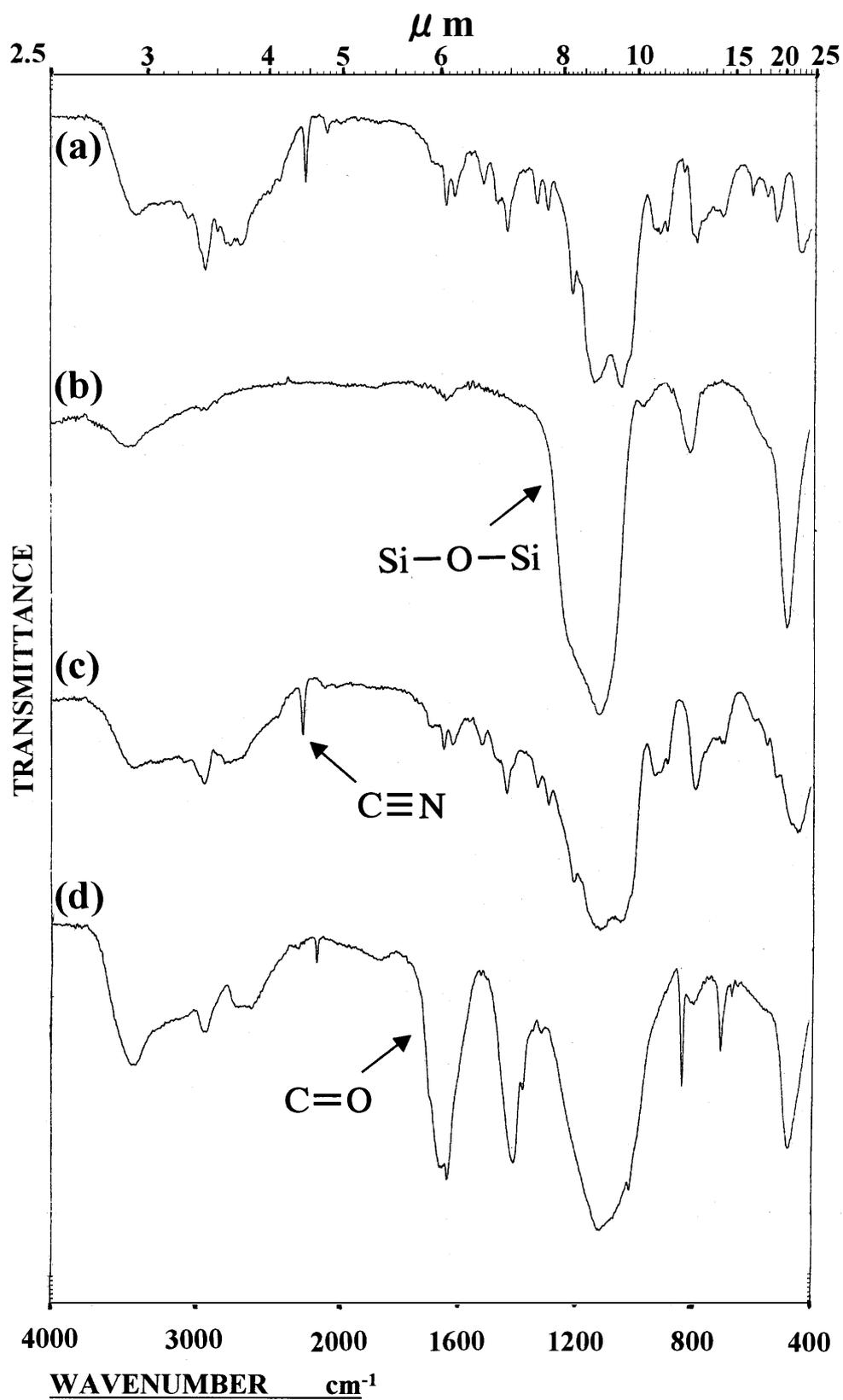


Figure 3. IR spectra of (a) TECS, (b) 15 nmφ SiO₂ spheres, (c) CN-terminated SiO₂ spheres, and (d) COOH-terminated SiO₂ spheres ; see text for details.

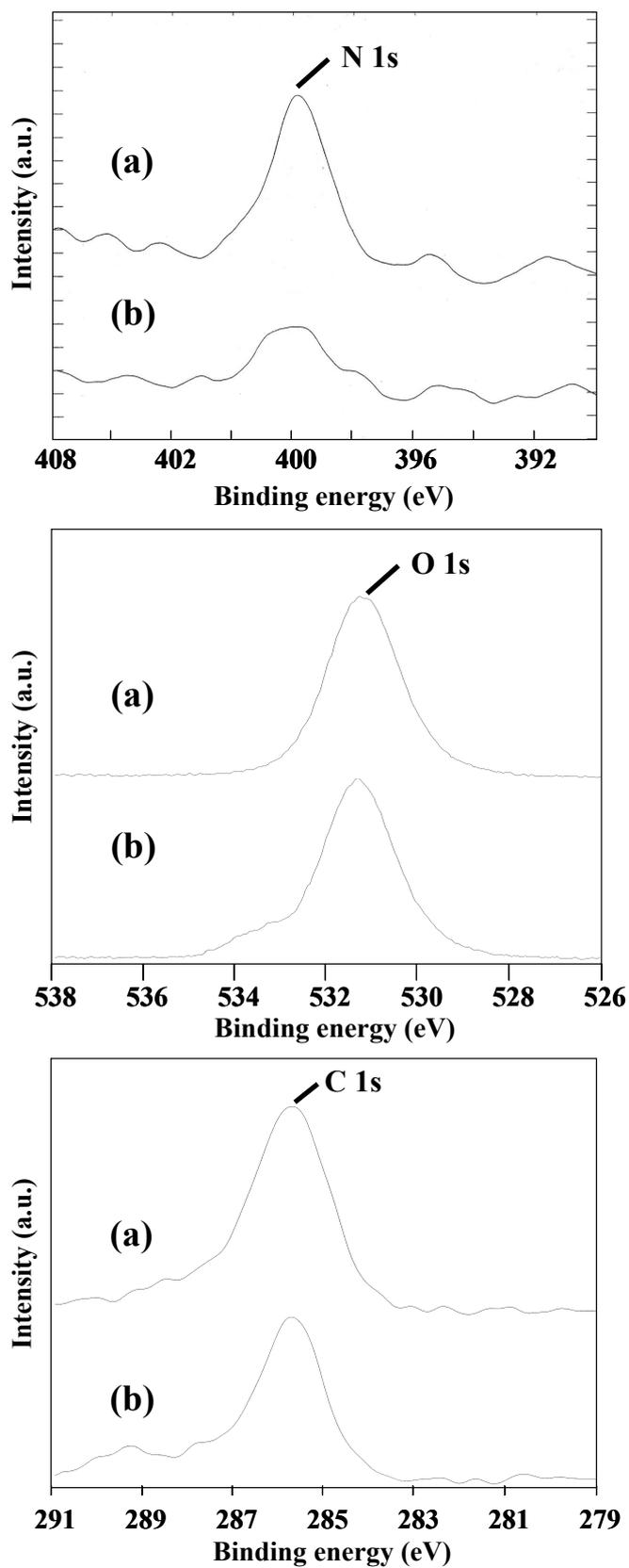


Figure 4. XPS spectra for the surface of a TECS-treated Si substrate ; (a) before and (b) after further treatment with t-BuOK.

spectrum of O 1s was assigned to the surface oxide layer (SiO₂) on the wafer. Broad band at 533.4 eV was observed after oxidation and was assigned to the oxygen atoms of COOH groups (532.8 eV (C=O) and 534.5 eV (C-O-H)³⁻⁶). The spectrum of C 1s (285.5 eV) was considered to be a mixture of two peaks from carbon atoms of CH₂ (285.0 eV³⁻⁶) and CN (286.0 eV³). The intensity of C 1s was also reduced by oxidation. Additionally, a weak spectrum centered at 289.2 eV was observed after oxidation, and was assigned to C 1s of COOH (289.5 eV³⁻⁶). These observations suggest CN group was oxidized to COOH group with a loss of a carbon atom of CN group as shown in Fig. 2. The yield of COOH groups estimated from the N 1s spectra was approximately 75 %, which is slightly lower than the reported yield, 86 %.⁷

Micropatterning of SiO₂ spheres on SAM

Carboxyl-group-terminated SiO₂ spheres were sonicated for 10 min in tetrahydrofuran or dichloromethane, and this solution was refrigerated to -20 °C for 1 h. N,N'-dicyclohexylcarbodiimide (DCC, Kishida Chemical Co., Ltd.) was added to this solution as a condensing agent⁸⁻⁹, and the temperature of the solution was increased slowly to 20 °C. A phenyl / silanol-patterned SAM substrate was then immersed in this solution for 2 h. The solution temperature was further raised and kept at 25 °C for 2 h.

After having been rinsed in acetone, the patterned-SAM substrates were observed with scanning electron microscopes (S-510, Hitachi Ltd. and JSM 6301F, JEOL Ltd.) and an atomic force microscope (Nanoscope E, Digital Instruments). SiO₂ spheres were observed predominantly in the silanol-group regions (Figs. 5, 6 and 7), which indicates that carboxyl groups on the SiO₂ sphere surfaces were adhered to silanol groups of the SAM selectively. In order to further verify the selective presence of SiO₂ spheres, these were attached to SAMs formed on an alumina substrate (Kyocera Co. Ltd.). Energy dispersive x-ray analysis (EMAX-1700, Horiba Ltd.) of the spheres adhered to silanol surfaces clearly revealed that they were SiO₂. The substrates with small SiO₂ spheres (A : 15 nm ϕ) were further sonicated in water, ethyl alcohol and acetone for 10 min, respectively, but removal of SiO₂ spheres was not observed. This observation firmly suggests that the bonds between SiO₂ spheres and silanol groups of SAM, possibly ester bonds, were strong enough to keep them adhered to each other during sonication, although preliminary attempts to directly detect the interfacial chemical bonds using IR and XPS (X-ray photoelectron spectroscopy) have not been successful. Strong bonds between SiO₂ spheres and SAM were confirmed to be present in an ambient atmosphere for more than two months.

In order to verify the formation of ester bonds between carboxyl groups and silanol groups, bromopropionic acid, whose molecule has a carboxyl group at one end and a bromo group at the other, was reacted with silanol groups of a silicon substrate using the same reaction scheme as we used to attach SiO₂

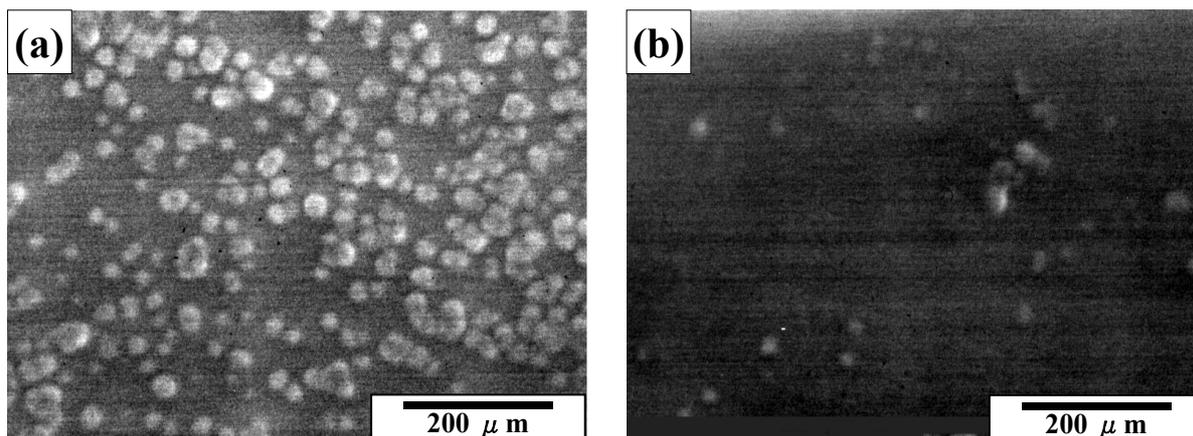


Figure 5. FE-SEM photographs of small SiO_2 spheres ($A : 15 \text{ nm}\phi$) arranged in (a) a hydrophilic silanol region and (b) a hydrophobic phenyl region of PTCS-SAM.

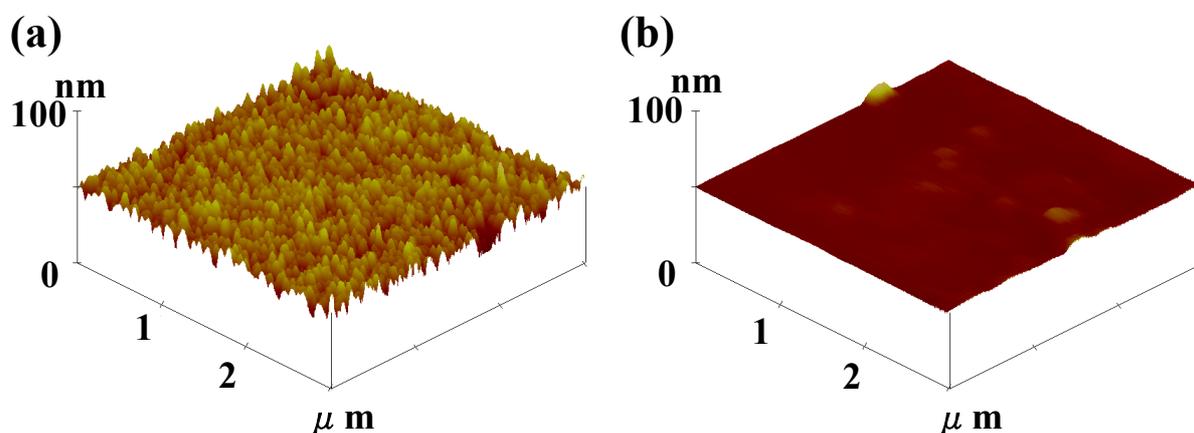


Figure 6. AFM images of small SiO_2 spheres ($A : 15 \text{ nm}\phi$) arranged in (a) a hydrophilic silanol region and (b) a hydrophobic phenyl region of PTCS-SAM.

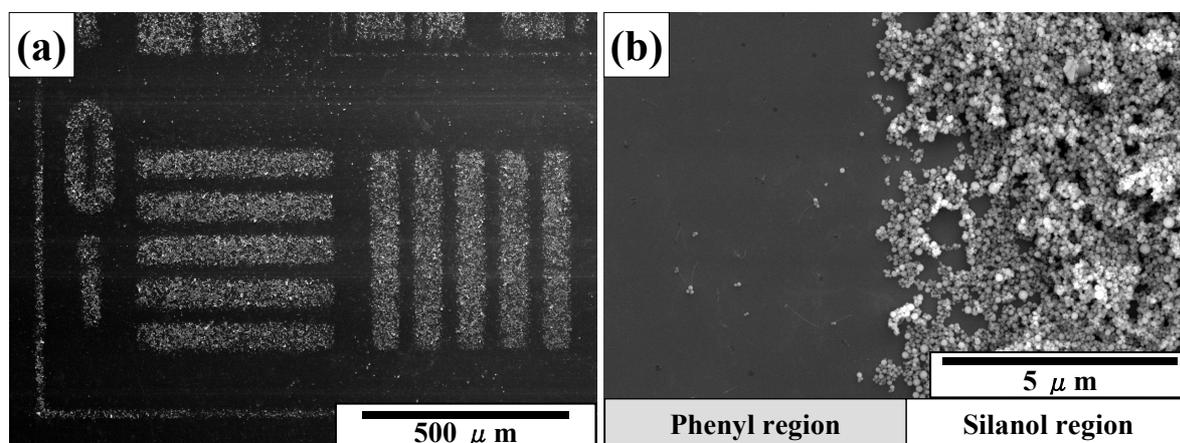


Figure 7. (a) SEM photograph of large SiO_2 spheres ($B : 500 \text{ nm}\phi$) arranged on a patterned SAM and (b) a magnified area of (a) showing selective adhesion of spheres to a hydrophilic silanol region.

spheres to silanol groups. After having been sonicated in acetone for 5 min, the substrate surface was analyzed by XPS. The spectrum corresponding to Br 3d binding energy centering at 74.35 eV was observed (Fig. 8). Although the observed binding energy is higher than that of KBr, this chemical shift must have been caused by carbon atoms neighboring bromine atoms.¹⁰ Since bromo groups can not react directly with silanol groups under the present conditions, the XPS result firmly indicates that carboxyl groups of bromopropionic acid reacted with silanol groups to form possible ester bonds.

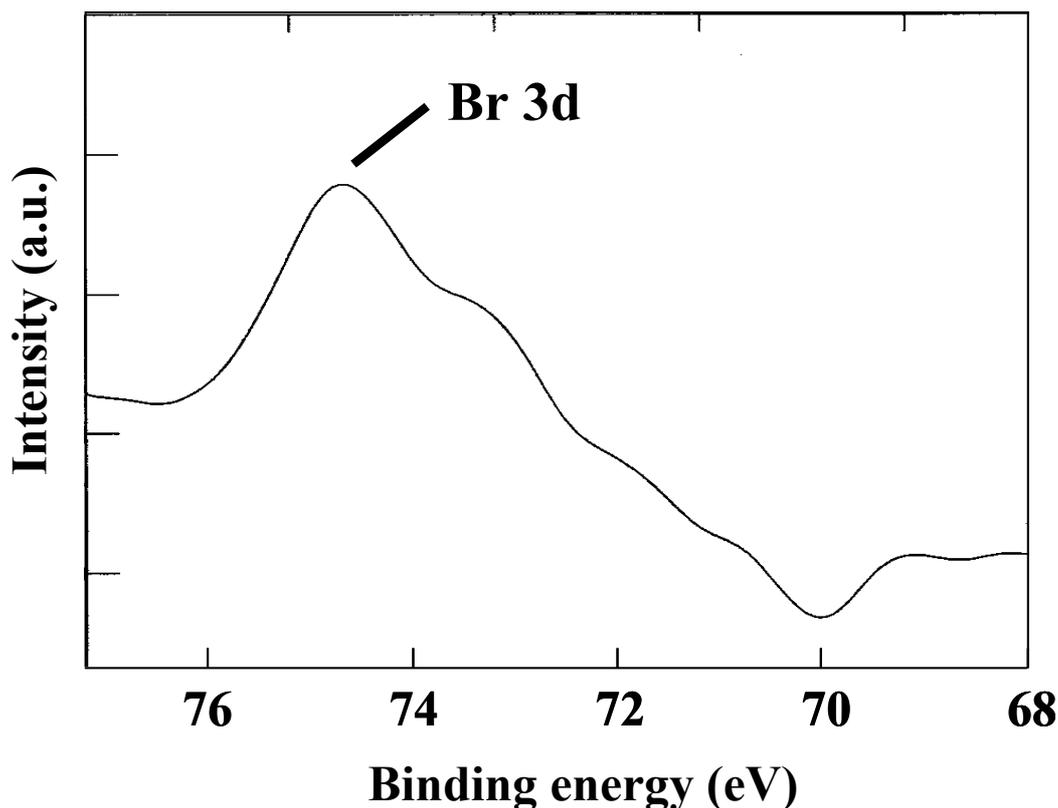


Figure 8. XPS spectrum of Br 3d for the surface of a bromopropionic acid-treated Si substrate.

Even though the selectivity of the SiO₂ sphere arrangement is fairly good, the number density of SiO₂ spheres on the silanol surface is rather low compared to our initial expectation for a two-dimensionally close-packed structure. Moreover, a small number of SiO₂ spheres can also be observed on hydrophobic phenyl surfaces (Figs. 5b and 6b). This finding is thought to be associated with the quality of the SAMs. Chemisorption of organosilanes bearing long alkyl “R” substituents leads to the formation of close-packed, ordered SAMs, having relatively few defects due to stabilization of the film structure by attractive van der Waals interactions between adjacent “R” chains.¹¹ In contrast, organosilanes bearing only simple aromatic “R” lack this stabilizing interaction and chemisorb in a more random fashion, producing more loosely-packed, higher defect-density SAMs.¹² Defects not bearing silanols on the hydrophilic surfaces

would not attract SiO₂ spheres, and unreacted silanols remaining at such defects on the hydrophobic phenyl surfaces would provide sites for the adhesion of SiO₂ spheres. Accordingly, it seems to be necessary to control the quality and uniformity of SAMs for the perfectly selective arrangement of particles.

In the case of large SiO₂ spheres (B : 500 nm ϕ), their selective adsorption to the silanol regions was also observed. However, more than 90 % of spheres were easily removed by 1 min sonication in acetone. Whether SiO₂ spheres are strongly adhered to a SAM substrate seems to be associated with the size of particles which would cause the difference in the relative amount of silanol groups on the sphere surfaces. Accordingly, thermogravimetric analyses were carried out to evaluate the amount of surface carboxyl groups. The results shown in Fig. 9 clearly indicate that the weight loss percentage of small spheres A is much larger than that of large spheres B. Weight loss observed at room temperature to ~ 100 °C is considered to be due to the desorption of physisorbed water.

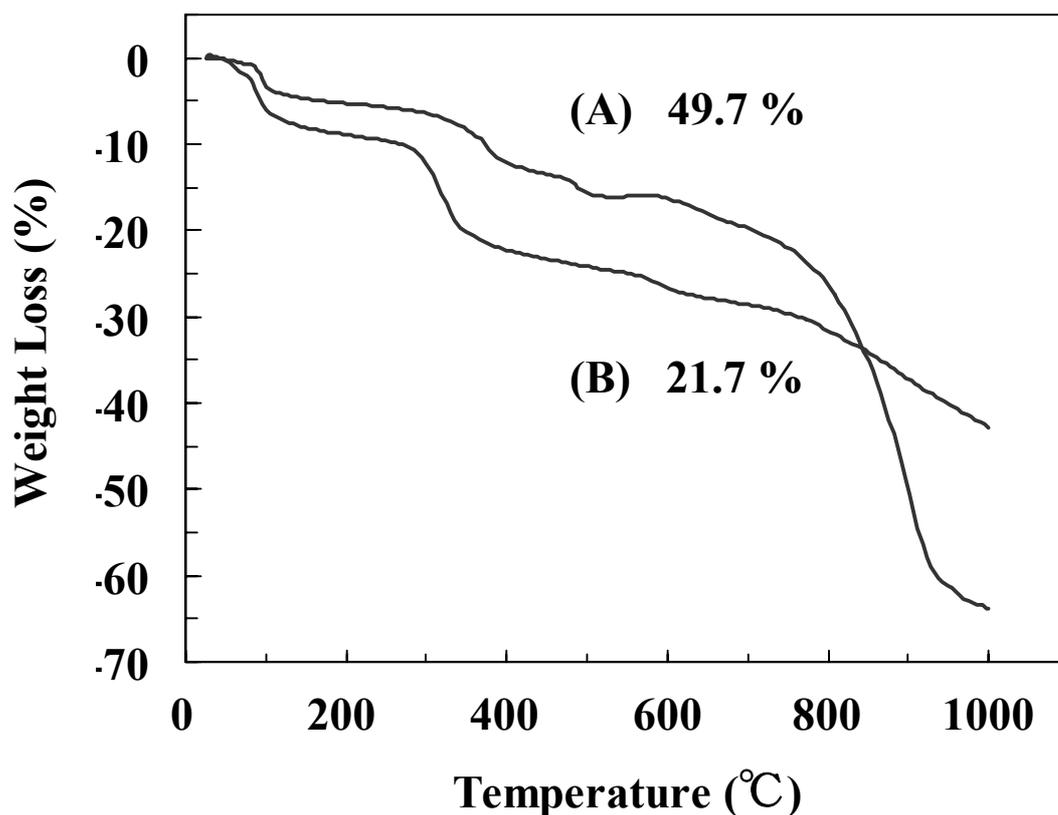


Figure 9. Thermogravimetric analyses of SiO₂ spheres (A : 15 nm ϕ , B : 500 nm ϕ).

The density of carboxyl groups on the sphere surfaces can then be estimated from the weight change shown in Fig. 9 assuming the SiO₂ spheres to be perfectly spherical and uniform in size. The estimated

densities of carboxyl groups for spheres A and B were $3.2 \times 10^{15} \text{ cm}^{-2}$ and $4.7 \times 10^{16} \text{ cm}^{-2}$, respectively. This estimation indicates that the difference in adhesion strength of spheres and SAM for two kinds of spheres should not have been caused by the difference in the density of carboxyl groups. Sphere size and weight would be more responsible for the adhesion strength.

Conclusions

In consequence, nano-sized SiO_2 spheres were successfully arranged in the silanol regions of PTCS-SAMs. The technique developed in the present study can be applied to the arrangement of various kinds of inorganic particles. However, this report would only give a first step towards the realization of perfect sphere arrangement, and further efforts to improve the technique must be made to realize nano / micro devices in the future.

References

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4.4 Novel surface modifications of SAMs and site-selective deposition of particles to form close-packed particle layers using chemical reactions

Micropattern of close-packed particle layer was fabricated through the formation of siloxane bonds between particles and SAMs. Furthermore, SAMs were modified by the AFM lithography technique or a mechanical modification technique with a diamond tip and micropatterns of particles were fabricated on the patterned SAMs.

Micropatterning of SiO₂ spheres on SAM using acid or base

Silanol groups were reported to form siloxane (Si-O-Si) easily through dehydration in the presence of an acid or base.¹ We attempted to form siloxane bonds between silanol groups of silica spheres and silanol groups of SAMs using (a) hydrochloric acid, (b) sulfuric acid, and (c) sodium hydroxide (Fig. 1). Silica spheres (500 nm ϕ , powder, Admatechs Co., Ltd., SO-E2) were sonicated in a hydrochloric acid solution, a sulfuric solution, or a sodium hydroxide solution for 10 min for dispersion. Then, patterned SAMs were immersed in the solution for 5 min. After having been rinsed in acetone, the patterned-SAM substrates were observed with a scanning electron microscope (S-3000N, Hitachi Ltd.). Silica spheres were observed predominantly in the silanol regions of the SAM in all cases (Fig. 2), which indicates that silanol groups on silica sphere surfaces were adhered to silanol groups of the SAM selectively. The arrangement with hydrochloric acid exhibits the finest patterning of all our experiments, it was much denser than the previously reported one,² and spheres with different sizes appear to be closely packed two-dimensionally. This

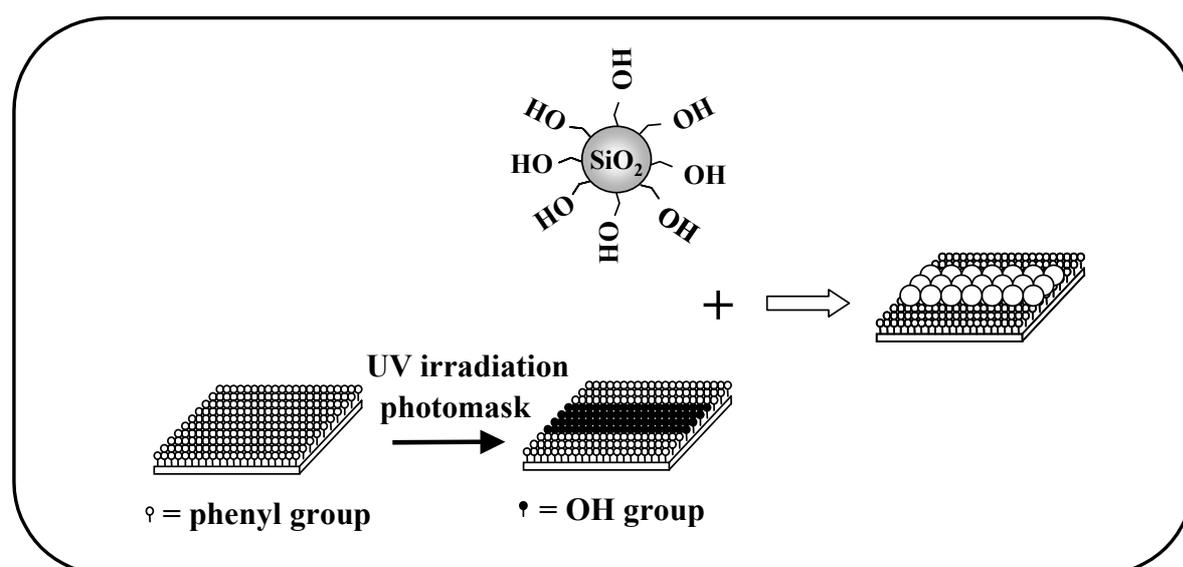


Figure 1. Conceptual process of arranging silica spheres on a SAM.

close-packed structure is very interesting and must be associated with the formation of siloxane bonds among silica spheres themselves as well as between spheres and a SAM. In contrast, many by-products were observed selectively on silanol surfaces for the case of sodium hydroxide; energy-dispersive X-ray analysis (EDAX Falcon, EDAX Co. Ltd.) indicated that sodium hydrogencarbonate (NaHCO_3) was possibly precipitated on silanol surfaces.

The substrates were further sonicated in acetone for 10 min, but the removal of silica spheres was not observed. This observation strongly suggests that the bonds between silica spheres and silanol groups of SAM, possibly siloxane bonds, are strong enough to keep them adhered to each other during sonication. Ester bonds between silica spheres and SAM could not maintain their bonds during sonication.²

Surface modification of SiO_2 spheres

Silica spheres ($500 \text{ nm}\phi$) were immersed in a dicyclohexyl solution and sonicated for 10 min under a N_2 atmosphere for good dispersion. One volume percent trichloroethoxysilane (TCES) was added to the dicyclohexyl solution under a N_2 atmosphere, and the solution was stirred gently for 10 min in order to chemisorb TCES to SiO_2 sphere surfaces. SiO_2 spheres with TCES were centrifuged several times to remove unreacted TCES

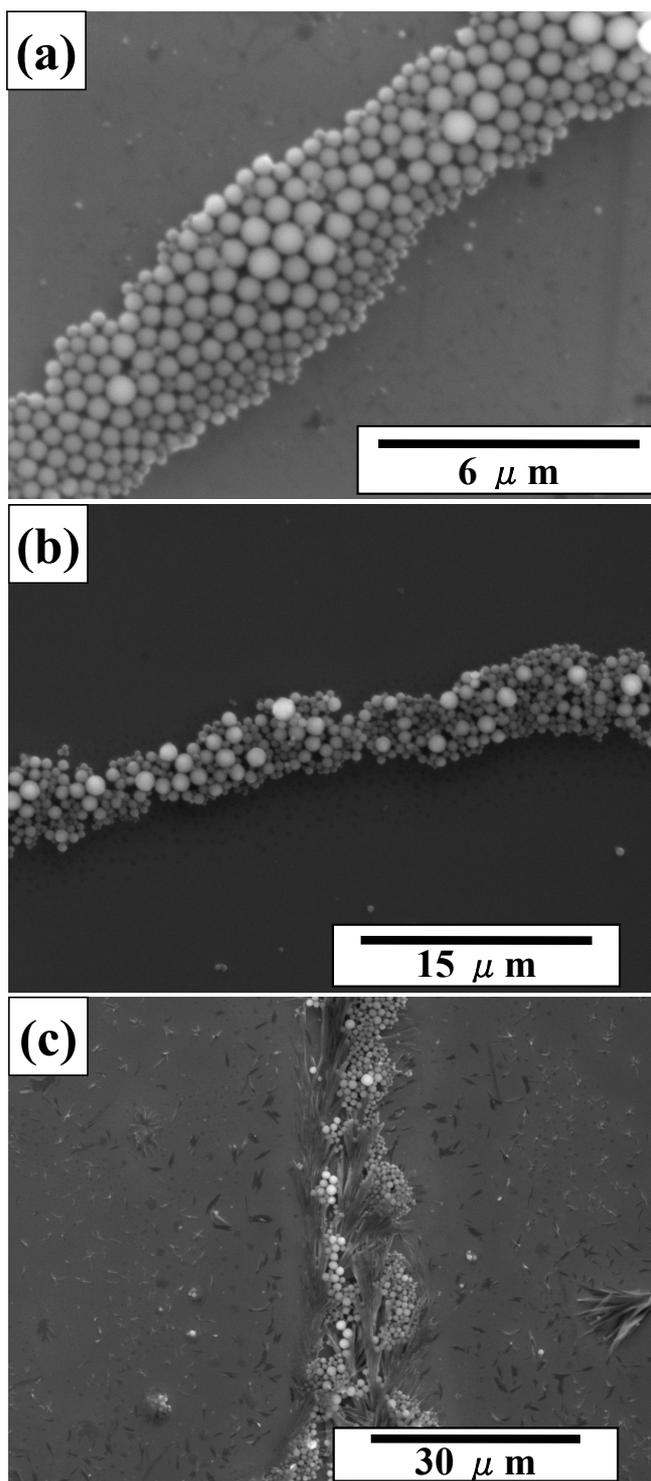


Figure 2. SEM photographs of silica spheres arranged on patterned SAMs using (a) hydrochloric acid, (b) sulfuric acid and (c) sodium hydroxide.

with dicyclohexyl. SiO₂ spheres with TECS were then baked at 120 °C for 5 min to remove residual solvent and to promote chemisorption of the TCES.

SiO₂ spheres with TCES were further dispersed in a tetrahydrofuran solution containing potassium tert-butoxide (t-BuOK) and 18-crown 6-ether for 24 h under an ambient atmosphere in order to oxidize CN-groups to carboxyl groups.³ This reaction was initiated by deprotonation at a C-H adjacent to the nitrile, and an oxidative cleavage transformed the carbon α to the nitrile into the carboxyl group. The solution was centrifuged to remove tetrahydrofuran, and brown precipitate was obtained. It was further centrifuged several times using distilled water to remove t-BuOK, 18-crown 6-ether, and tetrahydrofuran; carboxyl-group-terminated SiO₂ spheres were finally obtained after centrifugation. These spheres were arranged on patterned SAMs using AFM lithography and a diamond tip.

Surface modification of SAMs with AFM probe and arrangement of SiO₂ spheres

A source measure unit (SMU Model 236, Keithley) was installed in the AFM (Nanoscope E, Digital Instruments) in order to control the current flowing through the probe and the SAM. PTCS-SAMs were biased positively, and scanned with the AFM probe in constant current mode (50 nA), and the scanned area

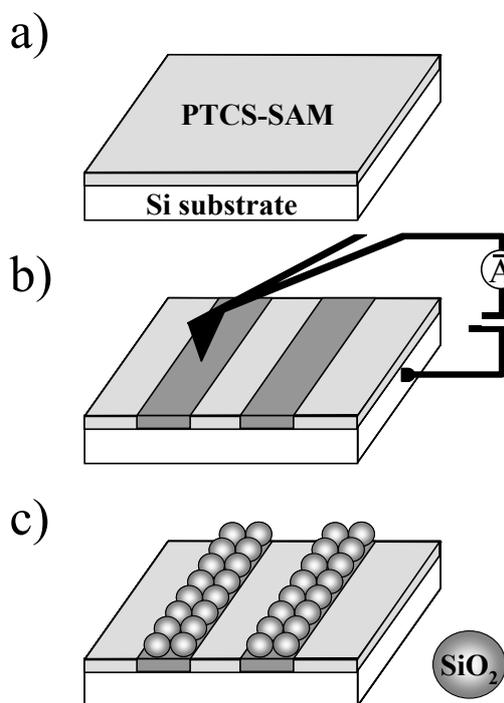


Figure 3. Schematic illustration of AFM lithography and sphere arrangement on patterned SAM.

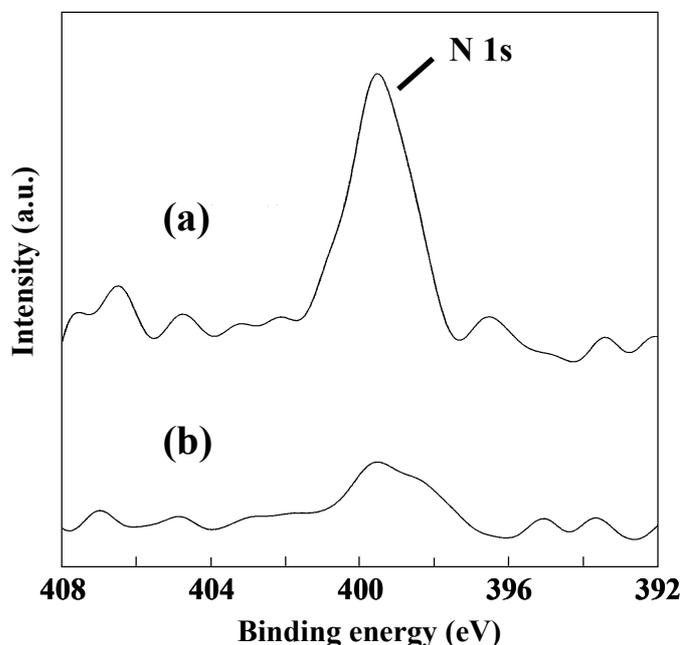


Figure 4. XPS spectrum of N 1s for the surface of a TCES-treated Si substrate (a) before and (b) after AFM lithography.

was used as a template for sphere arrangement (Fig. 3). Phenyl groups were modified to silanol groups by an electric current.⁴ In order to verify the modification of the SAM surface, cyano-group-terminated SAM was prepared using TCES, and scanned with the AFM probe in constant current mode. SAMs were evaluated by X-ray photoelectron spectroscopy (XPS) (ESCALAB 210, VG Scientific Ltd.). The X-ray source (MgK α , 1253.6 eV) was operated at 15 kV and 18 mA, and the analysis chamber pressure was $1-3 \times 10^{-7}$ Pa. The spectrum peak corresponding to the N 1s binding energy centered at 399.7 eV was observed for the surface of the TCES-treated Si substrate on which TCES-SAM was formed (Fig. 4). The intensity of this peak decreased greatly after the substrate was scanned by the AFM probe. This showed that ethylene chains and/or cyano groups were decomposed by AFM lithography.

Carboxyl-group-terminated silica spheres were sonicated for 10 min in dichloromethane, and this solution was refrigerated to -20 °C for 1 h. N,N'-dicyclohexylcarbodiimide (DCC, Kishida Chemical Co., Ltd.) was added to this solution as a condensing agent,^{5,6} and the temperature of the solution was increased slowly to 20 °C. A phenyl/silanol-patterned SAM substrate was then immersed in this solution for 2 h. The solution temperature was further raised and held at 25 °C for 2 h. After rinsing in acetone, the patterned SAM substrates were observed with a scanning electron microscope. Silica spheres were observed predominantly in the silanol regions (Fig. 5), which indicates that carboxyl groups on the silica sphere surfaces were adhered selectively to the silanol groups of the SAM. The AFM lithography technique was shown to be useful for sphere arrangement in this experiment.

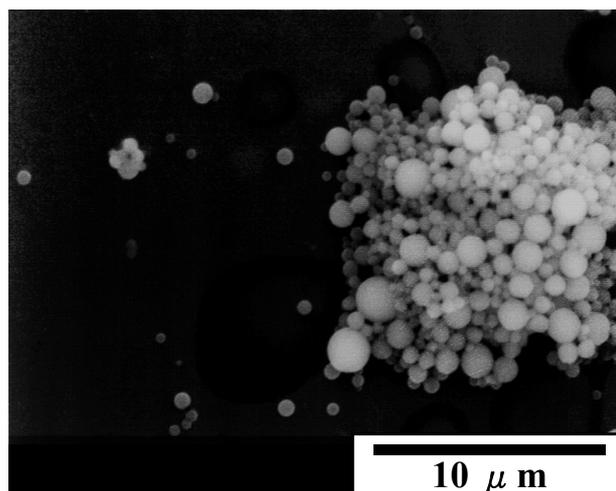


Figure 5. SEM photograph of silica spheres arranged on patterned SAMs by AFM lithography.

Surface modification of SAMs with diamond tip and arrangement of SiO₂ spheres

The diamond tip was contacted to a SAM surface lightly and traced with low contact pressure in order to modify the SAM surface. Phenyl groups were broken mechanically by contact pressure with the diamond tip, and they possibly changed into silanol groups. The diamond tip was used to avoid contamination from a metal tip and the influence of a chemical reaction between the tip and the SAM. After modification using the diamond tip, the patterned SAM was immersed into a dichloromethane solution containing

carboxyl-group-terminated silica spheres. DCC was then added in the same manner as that for the patterning using AFM lithography. After rinsing in acetone, the patterned SAM substrates were observed with a scanning electron microscope. Silica spheres were observed predominantly on silanol surfaces (Fig. 6), which indicates that carboxyl groups on silica sphere surfaces were strongly adhered selectively to silanol groups of the SAM. This result suggests the possibility of mechanical surface modification using a diamond tip, and this technique can be applied to modification of the SAM for sphere arrangement.

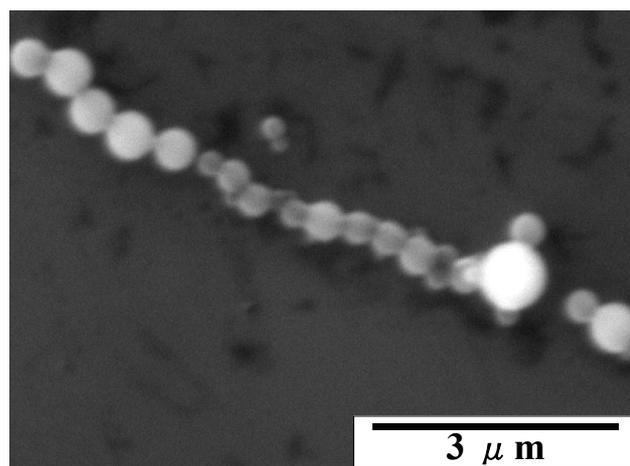


Figure 6. SEM photograph of silica spheres arranged on patterned SAMs by a diamond tip.

Conclusions

Silica spheres were arranged on silanol surfaces of SAMs selectively in the presence of an acid or base. A two-dimensional close-packed arrangement of spheres was achieved by using hydrochloric acid to form siloxane bonds among silica spheres and SAMs. The AFM lithography technique and mechanical modification with a diamond tip were also successfully applied in preparing templates for the selective arrangement of silica spheres on silanol surfaces through ester bond formation.

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4.5 Site-selective deposition and precise arrangement of particles in the solution

We improved our patterning method to realize precise arrangement of particles. Particles were arranged on silanol groups of SAMs to form close-packed particle wires. Each particle was put on desired position modified by AFM lithography. Furthermore, micropattern of close-packed particle layer was fabricated using electrostatic interaction between particles and SAMs.

Preparation of a SAM patterned with octadecyl groups and amino-groups. The patterned OTS-SAM which has octadecyl groups and silanol groups was immersed in a toluene solution containing 1 vol% APTS (aminopropyltriethoxysilane) in air for 1 h. APTS molecules combined to silanol groups of SAM and hence, octadecyl / amino groups patterned SAM was fabricated. OTS-SAM exhibited a water contact angle of 96° , while that of the amino surface was 28° . These observations indicated successful fabrication of octadecyl / amino-groups patterned SAM.

Surface modification of SiO₂ particles with carboxyl groups. Silica particles ($1\ \mu\text{m}\phi$, HIPRESICA UF, UNK, Ltd.) were immersed in a dicyclohexyl and sonicated for 10 min under a N₂ atmosphere for good dispersion. 1 vol% of trichlorocyclohexylsilane (TCES) was added to the dicyclohexyl solution under a N₂ atmosphere, and the solution was stirred gently for 30 min in order to chemisorb TCES onto the SiO₂ particle surfaces. SiO₂ particles with TCES were centrifuged several times to remove unreacted TCES using dicyclohexyl.

The SiO₂ particles with TCES were further dispersed in a tetrahydrofuran solution containing potassium tert-butoxide (t-BuOK) and 18-crown 6-ether for 48 h under an ambient atmosphere to oxidize the CN-groups to carboxyl groups.¹ The solution was centrifuged several times using distilled water to remove t-BuOK, 18-crown 6-ether, and a tetrahydrofuran. SiO₂ particles modified with carboxyl groups were thus obtained.

SiO₂ particles covered by silanol groups or carboxyl groups were arranged selectively in silanol regions or amino regions of SAM using interactions between particles and SAMs. Zeta potentials of SiO₂ particles that have silanol groups and SiO₂ particles modified by carboxyl groups were measured (Zetasizer 3000HSA, Malvern Instruments Ltd.) as shown in Fig. 1. Zeta potentials measured in aqueous solutions (pH = 7.0) for the surface of silicon substrate covered with silanol groups, phenyl groups (PTCS) and amino groups (APTS) are $-38.23\ \text{mV}$, $+0.63\ \text{mV}$ and $+22.0\ \text{mV}$, respectively.²

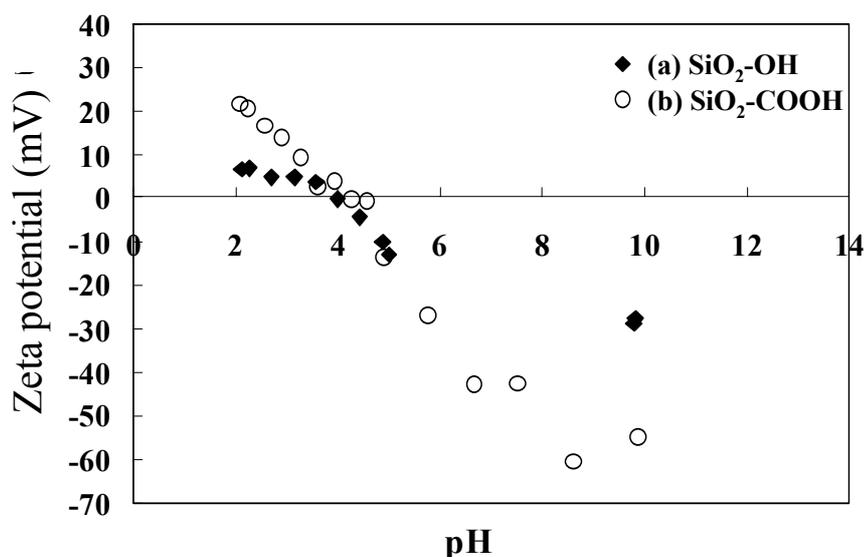


Figure 1. Zeta potential of (a) SiO₂ particles and (b) SiO₂ particles modified with carboxyl groups.

Fabrication of particle wires employing selective arrangement process.

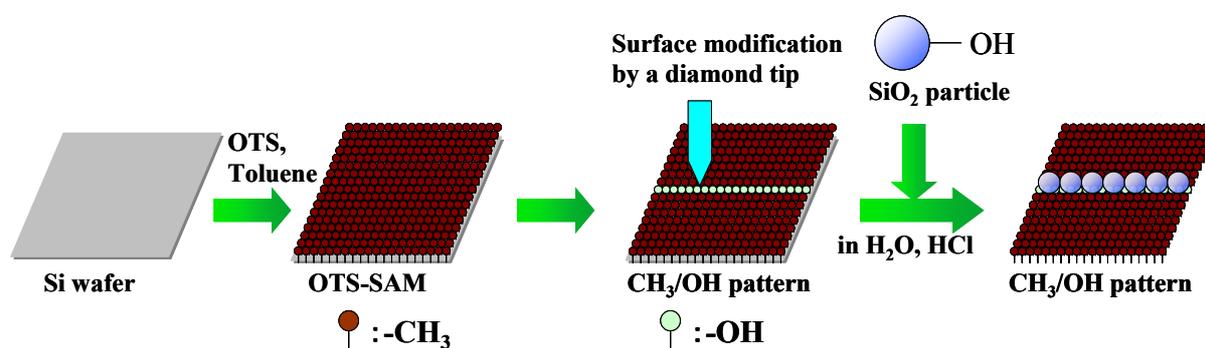


Figure 2. Conceptual process for fabrication of a particle wire on a patterned SAM modified by a diamond tip.

OTS-SAM was modified by a diamond tip to form a line of silanol groups of approximately 0.5 μm width (Fig. 2). The diamond tip was contacted to OTS-SAM surface lightly and traced with low contact pressure in order to modify the SAM surface. The surface modified by a diamond tip, i.e., the white area in Figure 2 corresponds to silanol groups, showed low contact angle ($< 5^\circ$). This modified region was shown to be white compared with OTS-SAM region in a scanning electron micrograph (SEM; S-3000N, Hitachi, Ltd.). Octadecyl groups were broken mechanically by contact pressure with the diamond tip, and they possibly changed into silanol groups. The diamond tip was used to avoid contamination from a metal tip and the influence of a chemical reaction between the tip and the SAM.

Patterned SAMs were immersed in the aqueous solution containing SiO₂ particles and a hydrochloric acid as a condenser³, rinsed in water, and were observed by a SEM. SiO₂ particles were observed on lines of silanol groups selectively indicating particles were successfully arranged well (Fig. 3(a)).

Because particles were not easily removed by sonication, it was judged that iloxane bonds had been formed by condensation of silanol groups between particles and a SAM.

It is clearly seen that the accuracy of particle arrangement has been improved compared to our former experiments.³⁻⁴ A double particle wire and a triple particle wire were likewise fabricated on wide silanol groups regions with about 1.4 μm and 2.2 μm in width, respectively (Fig. 3(b), (c)). The double particle wire that has a triangular lattice also demonstrates a high arrangement accuracy, though there is a defect in arrangement between seventh particle from left and eighth particle. Additionally, a curved double particle wire was fabricated on curved region of silanol groups. Curved double particle wires have not been reported previously, and they may have useful applications for an optical waveguide.

Accuracy of particle arrangement was evaluated from Fig. 3(a). Center position ((x_i, y_i) μm) of each particle was plotted to estimate the standard deviation (Fig. 4). The bottom left corner of Fig. 3(a) was set to be the origin of the x-y coordinate. The approximated straight line($f(x)$) and its slope (θ) are represented as follows.

$$f(x) = 0.0061x + 2.9609, \quad (1)$$

$$\cos \theta = 0.9940, \quad (2)$$

Standard deviation from the approximated straight line is described by the expression,

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

where n is the number of particles ($n=6$). We obtained $S = 0.0126$. The accuracy of particle arrangement in Fig. 3(b) and (c) was estimated by the same manner. Standard deviation of seven particles from left in an upper particle line and an bottom particle line in Fig. 3(b) were estimated to be $S = 5.66 \times 10^{-3}$ and $S = 3.84 \times 10^{-3}$. And standard deviation of an upper particle line, a middle particle line and a bottom particle line in Fig. 3(c) were estimated to be $S = 8.11 \times 10^{-4}$, 8.27×10^{-3} and 2.30×10^{-2} , respectively.

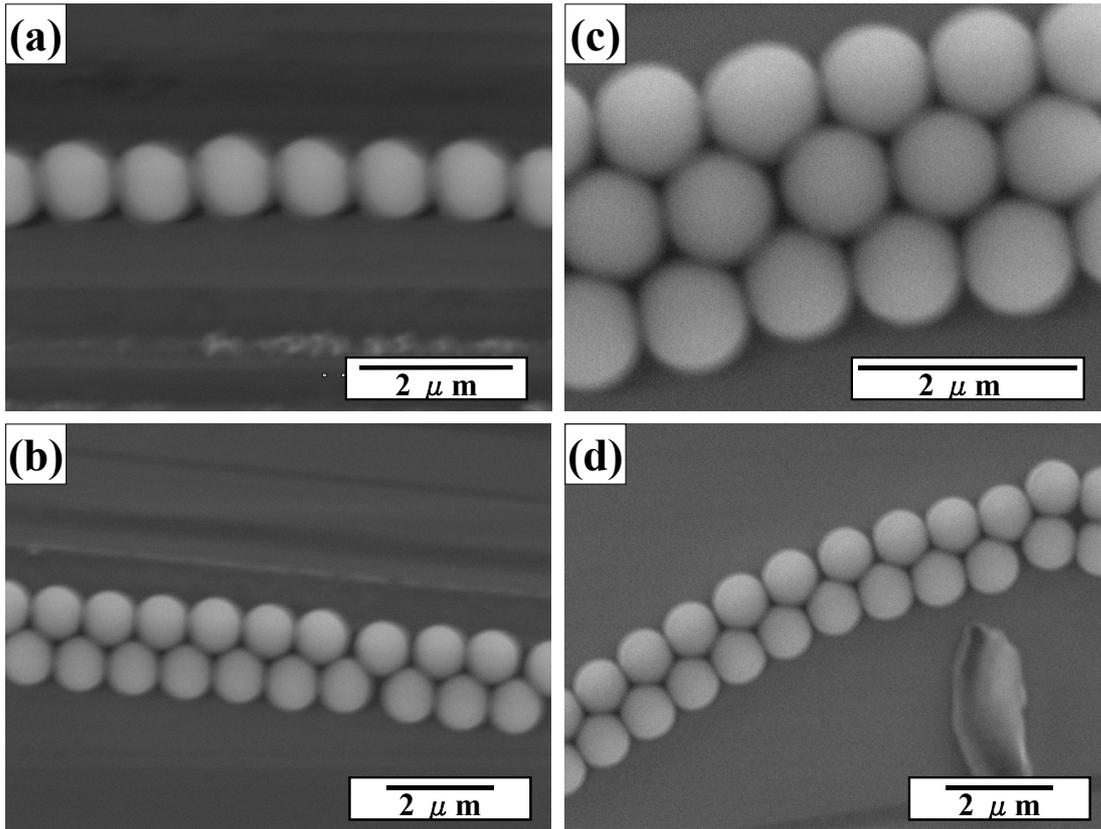


Figure 3. SEM micrographs of (a) a single particle wire, (b) a double particle wire, (c) a triple particle wire and (d) a curved double particle wire.

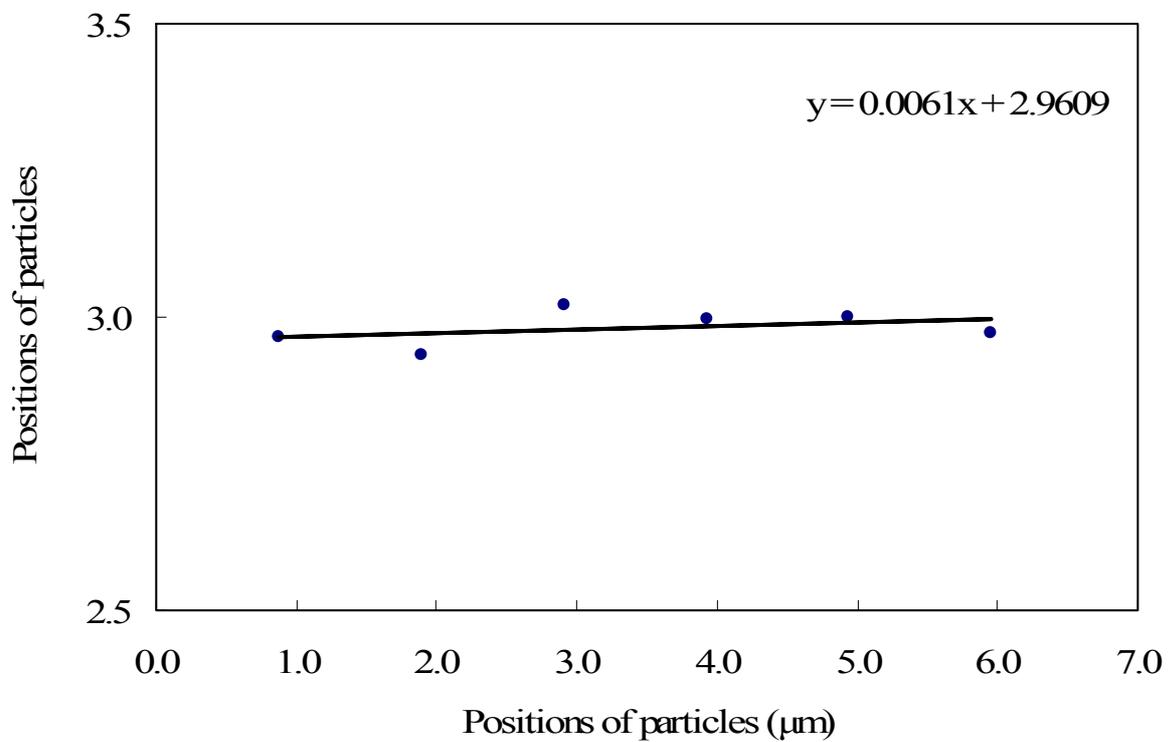


Figure 4. Positions of particles in Figure 3 a showing the accuracy of particle arrangement.

Precise arrangement of particles on small-area silanol sites modified by AFM lithograph.

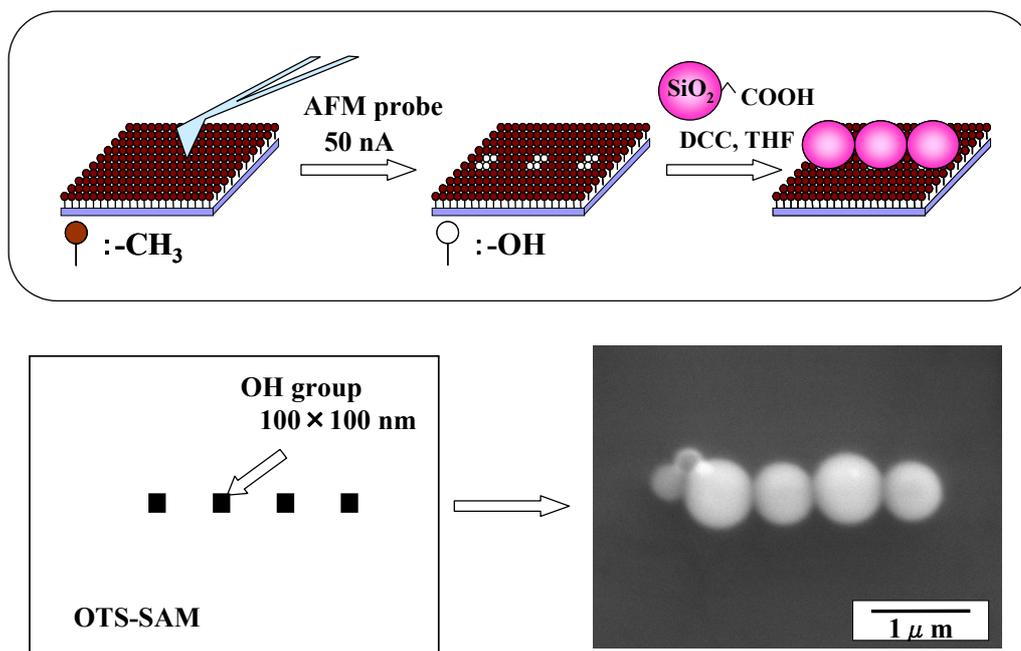


Figure 5. Conceptual process and SEM micrograph of particle arrangement on a patterned SAM modified by AFM lithography.

OTS-SAM was modified to silanol groups by an AFM (atomic force microscope, Nanoscope E, Digital Instruments) to control position of arrangement accurately (Fig. 5). A source measure unit (SMU Model 236, Keithley) was installed in the AFM in order to control the electric current passing through the probe and a SAM. The SAM was biased positively, and the AFM probe was scanned with constant current mode (50 nA), and the scanned area was used as a template for arrangement. Scanning area (100 nm × 100 nm) was set smaller than the diameter of the particles (500 nm ϕ), to facilitate precise arrangement of particles.

SiO₂ particles (500 nm ϕ , powder, Admatechs Co., Ltd., SO-E2) modified with carboxyl groups were sonicated for 10 min in tetrahydrofuran or dichloromethane, and this solution was refrigerated to -20 °C for 1 h. N,N'-dicyclohexylcarbodiimide was added to this solution as a condenser⁵⁻⁶ to form ester bonds between carboxyl groups of SiO₂ particles and silanol groups of a SAM.⁴ Modified OTS-SAM was then immersed in this solution for 2 h. The temperature of the solution was increased slowly to 25 °C and kept for 2 h. After having been rinsed in water, a SAM was observed by a SEM. Particles were arranged in silanol regions and line of particle was fabricated (Fig. 5). Two-dimensional arrangement with required features can easily be realized with this technique, though it takes a long time to modify a SAM with an AFM probe. Particles weren't removed easily from a SAM by sonication, indicating that ester bonds were formed by condensation. The accuracy of particle arrangement in Fig. 5 was estimated to be $S = 1.17 \times 10^{-2}$. This might be decreased by decreasing the dimension of each silanol region.

In order to verify the formation of ester bonds between carboxyl groups and silanol groups, bromopropionic acid, whose molecule has a carboxyl group at one end and a bromo group at the other, was reacted with silanol groups of a Si substrate using the same reaction scheme as we used to attach SiO₂ particles to silanol groups. After having been sonicated in acetone for 5 min, the substrate surface was analyzed by X-ray photoelectron spectroscopy (XPS; ESCALAB 210, VG Scientific Ltd., $1-3 \times 10^{-7}$ Pa, measurement area; 3 mm × 4 mm). The X-ray source (MgK α , 1253.6 eV) was operated at 15 kV and 18 mA. The spectrum corresponding to Br 3d binding energy centering at 74.35 eV was observed.⁴ Although the observed binding energy is higher than that of KBr, this chemical shift must have been caused by carbon atoms neighboring bromine atoms.⁷ Since bromo groups can't react directly with silanol groups under the present conditions, the XPS result firmly indicates that carboxyl groups of bromopropionic acid reacted with silanol groups to form possible ester bonds.

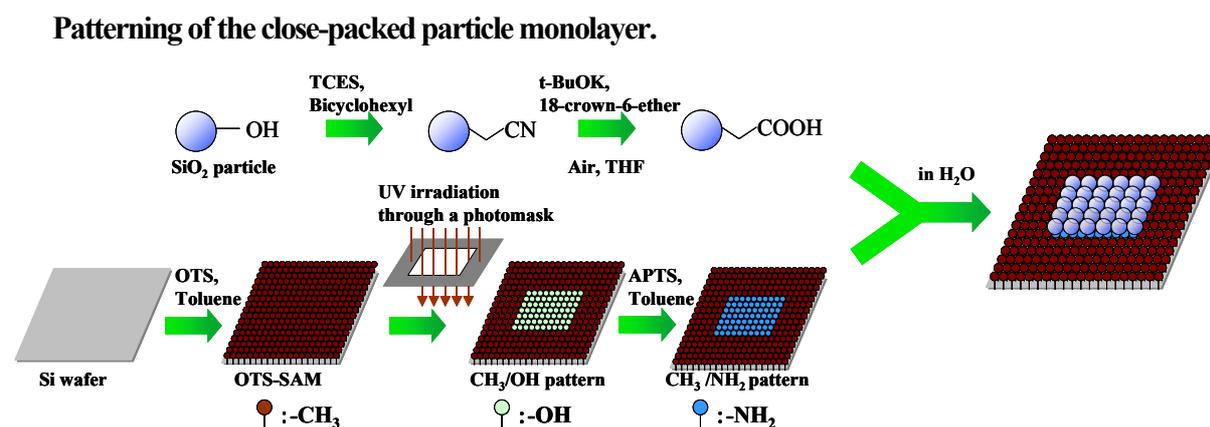


Figure 6. Conceptual process for patterning of the close-packed particle monolayer.

SiO₂ particles modified with carboxyl groups were dispersed in water. Octadecyl / amino-groups patterned SAM was then immersed in the solution for several minutes (Fig. 6). The substrate was rinsed with water and observed with a SEM. SiO₂ particles were observed in silanol regions selectively forming a close-packed mono-particle layer (Fig. 7 (a)). Boundaries between the mono-particle layer and octadecyl region is clearly observable, and a few particles are observed in octadecyl region. SiO₂ particles modified with carboxyl groups are charged negative, and amino groups of SAM are charged positive in water. Accordingly, particles are attracted to amino groups and form a mono-particle layer. Particles in the solution did not adhere to the mono-particle layer, since both the particles and the mono-particle layer have negative charges and repel each other. Particles were also deposited randomly in some areas (Fig. 7 (b)), and this suggests that it is difficult to obtain the pattern of the close-packed particle monolayer in a large area.

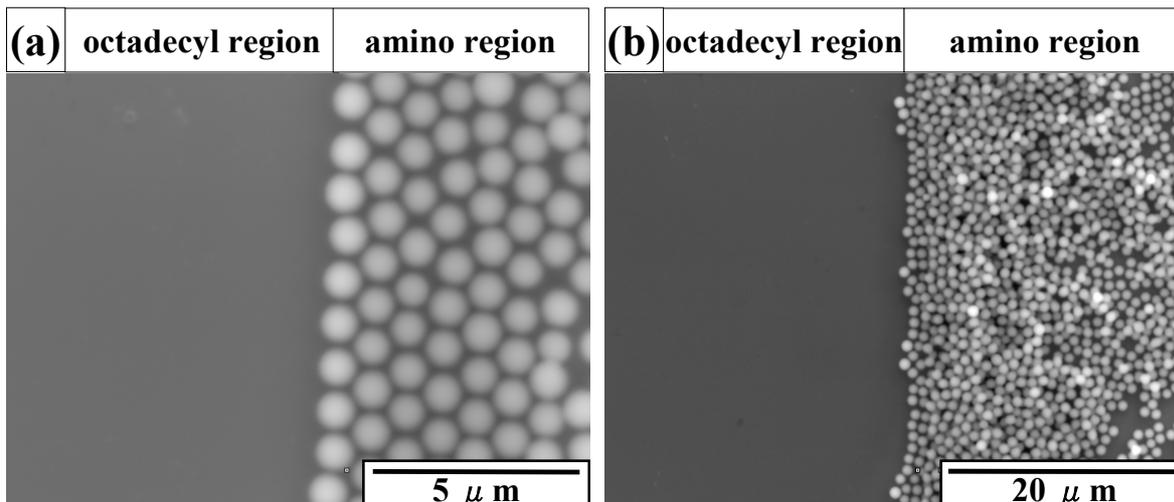


Figure 7. SEM micrographs of (a) a close-packed particle monolayer of SiO₂ particles modified with carboxyl groups formed in the amino region and (b) randomly deposited particles in the amino region.

Additionally, octadecyl / amino-groups patterned SAM was immersed in the solution containing non-modified SiO₂ particles for several minutes (Fig. 8). While SiO₂ particles were observed in silanol region predominantly, the feature edge acuity of the pattern was lower than that of the pattern in which SiO₂ particles modified with carboxyl groups was used. This demonstrates applicability of surface modification of SiO₂ particles with carboxyl groups. Furthermore, octadecyl / silanol-groups patterned SAMs were immersed in solutions containing SiO₂

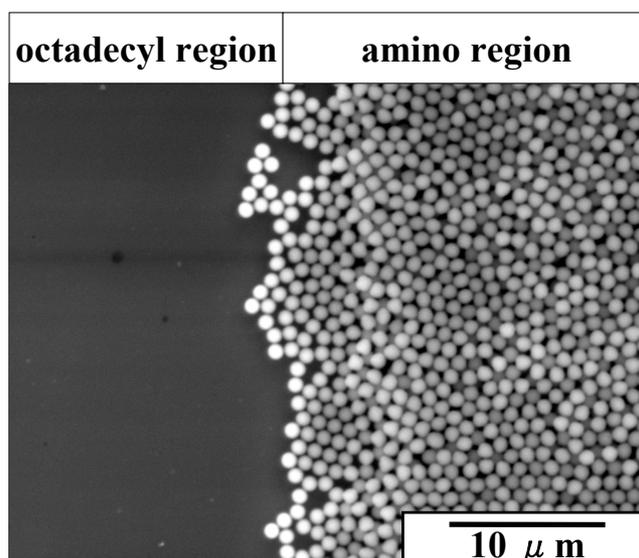


Figure 8. SEM micrograph of randomly deposited SiO₂ particles in the amino region.

particles modified with carboxyl groups or non-modified SiO₂ particles for several minutes, respectively. Particles were not adhered to either octadecyl groups or silanol groups. This means that the difference in surface potential between SiO₂ particles modified with carboxyl groups and amino groups of SAM accelerate the adhesion of particles to the amino groups. Particles were attracted and adhered to amino groups predominantly by electrostatic interactions between particles and SAMs and chemical bonds weren't formed because pure water was used as a solution with no condensation agent. Surface of SiO₂ particles modified with carboxyl groups and amino SAM must have changed into -COO^- and -NH_3^+ , respectively, in water to attract each other.

Conclusions

Surface modification of particles and SAM substrates was carried out to realize low-dimensional arrangement of SiO₂ particles. Micro-sized SiO₂ particles were arranged in silanol or amino regions selectively at room temperature by simply immersing the substrate in the solution. Precise arrangement of particles was achieved to form several kinds of particle wires, though it was difficult to arrange particles in a periodic manner in a large area. The arrangement technique we developed is considered to be promising for its potential applications to the future fabrication of electronic and photonic devices.

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4.6 Site-selective deposition and precise arrangement of particles using a liquid mold and its drying process

Micropatterns of particle assembly were fabricated using a liquid mold and its drying process. Particles were assembled to have regularity in their array by capillary force in the drying process. Patterns of a close-packed particle layer and particle wires were fabricated in the solution previously (chapter 4.2, 4.3, 4.4). Severe control of many factors was necessary to realize a close-packed structure and high accuracy because capillary force cannot be used in the solution. A close-packed structure can be easily obtained in our unique process compared with our previous process. Furthermore, non-close-packed structure was realized by the control of drying process.

Surface modification of SAMs and preparation of a colloidal solution for a liquid mold process.

OTS-SAM was modified to create two silanol regions (3 mm × 3 mm) and a line (10 μm) of silanol groups between them by UV irradiation (184.9 nm) for 2 h through a photomask (Fig. 1). Polystyrene particles in water (150 μl) (550 nmφ particle or 820 nmφ carboxylated particle, 10 wt%, dispersed in water, Seradyn Co., Ltd.) were further dispersed in ethanol (3 ml) or water (3 ml), and poured onto a patterned OTS-SAM. The contact angles of the ethanol solution or water solution measured 10-20 ° or 96 ° on the OTS-SAM, respectively, while they were saturated (contact angle < 5 °) on silanol groups. The droplets were observed to separate into two drops and a bridge of solution was formed on a silanol line. The droplets and the liquid bridge were used as a mold for fabrication of a two-dimensional pattern of colloid crystals. After evaporation of the solution, substrates were observed by a scanning electron microscope (SEM; S-3000N, Hitachi, Ltd.).

The dispersibility of particles in the solution is very important for particle assembly and high dispersibility is necessary to form a close-packed structure. The zeta potentials of particles dispersed in the solutions were examined by direct measurement of electrophoretic mobility using an electrophoretic light scattering spectrometer (Zetasizer 3000HS, Malvern Instruments Co., Ltd.). The zeta potentials of polystyrene particles (550 nmφ) in water, carboxylated particles (820 nmφ) in water, polystyrene particles in ethanol and carboxylated particles in ethanol were determined to be -38.3 mV, -50.2 mV, -53.9 mV and -44.0 mV, respectively. Surface modification by carboxyl groups decreased the negative zeta potential in both solutions.

Furthermore, particles in the ethanol had slightly low negative zeta potentials compared to those in water, i.e. the particles were slightly well-dispersed compared to those in water.

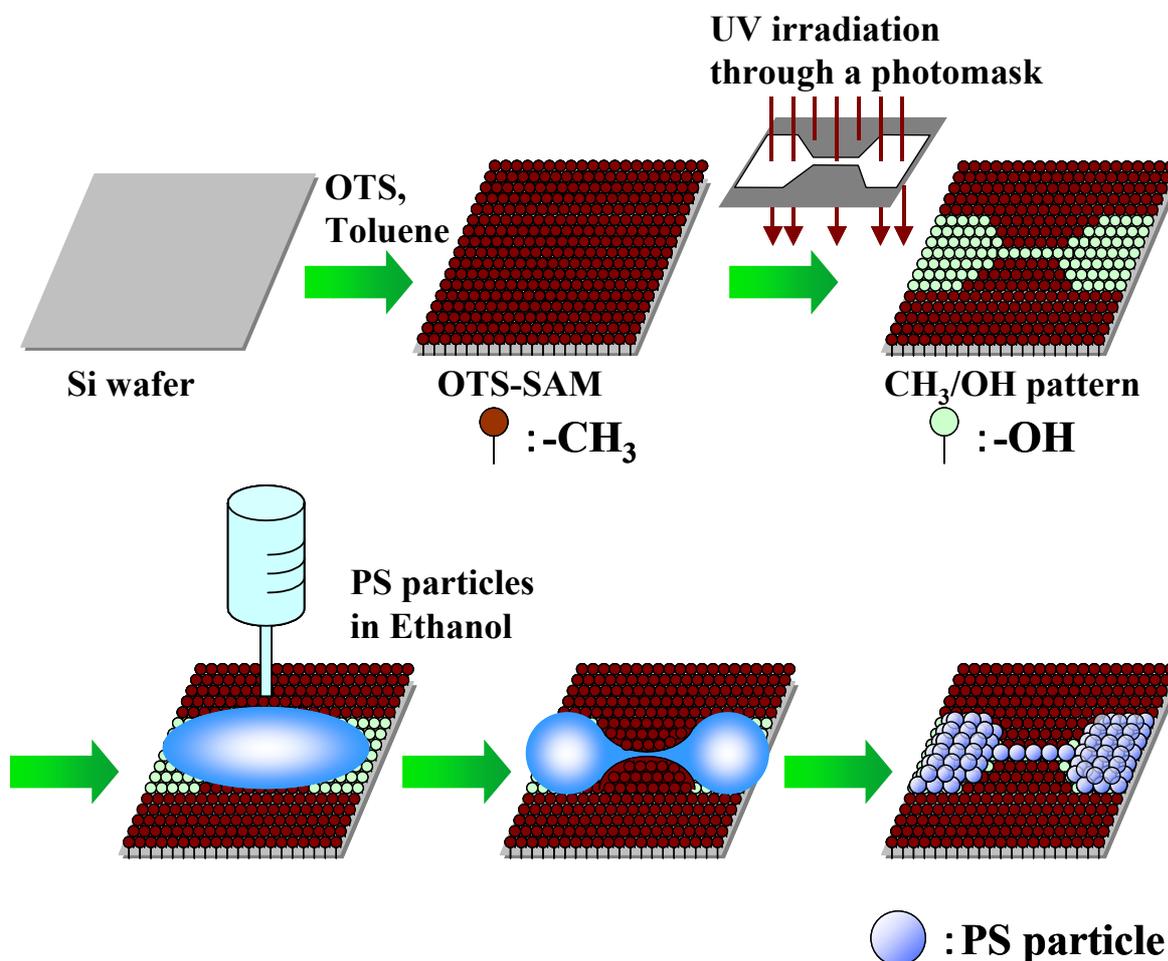


Figure 1. Conceptual process for fabrication of a particle wire using a patterned SAM and a liquid bridge.

Polystyrene particles in water were poured onto a patterned OTS-SAM, and observed after evaporation of the water. The water at the liquid bridge evaporated in about 24 h to form a particle wire, and droplets at the two ends completely evaporated in about 48 h. In this manner, particle wires constructed from a close-packed structure, i.e. triangular lattice, were produced from the water solution (Fig. 2a). The middle of a particle wire was narrower than its end (Fig. 2b, c). The width of the particle wire does not depend on the width of the silanol line, but rather on the interfacial tensions between solution and substrate, solution and atmosphere, and

atmosphere and substrate. The silanol line was not used to decide the width of the particle wire, but rather the position of the liquid bridge and particle wire. Close-packed structures were also formed on large silanol regions (Fig. 2d, e). The right-hand area of Fig. 2d can be regarded as the $\{100\}$ plane of the fcc structure and the left-hand area can be regarded as the $\{111\}$ plane of the fcc structure or the $\{0001\}$ plane of the hcp structure. The close-packed structure was thus considered to be an fcc structure.

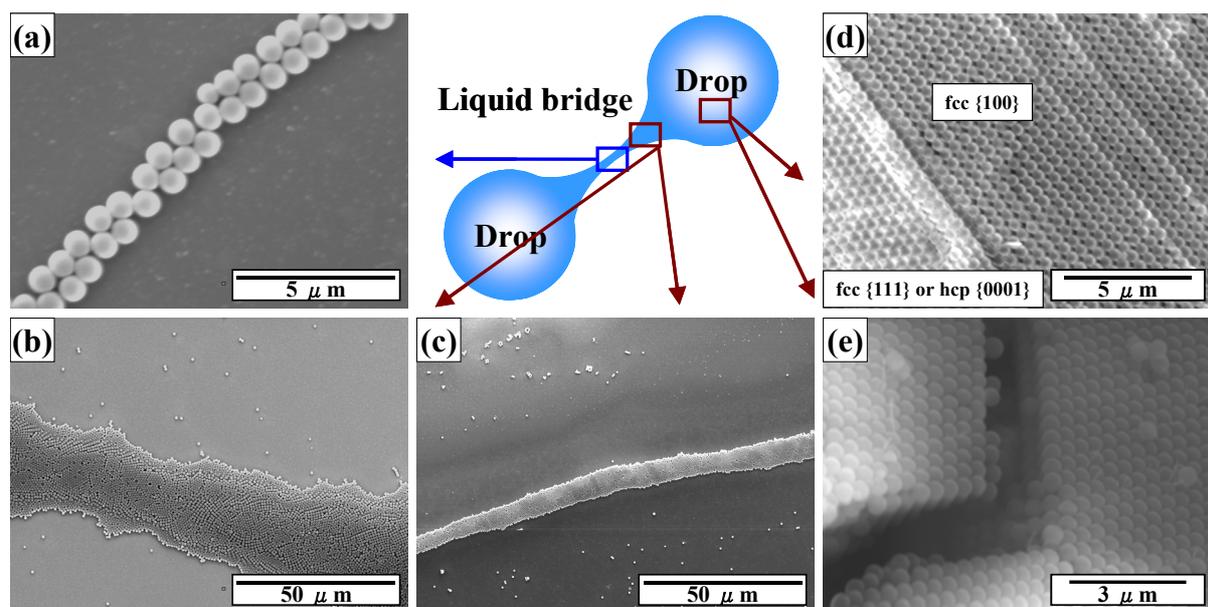


Figure 2. SEM micrographs of particle structures fabricated from aqueous solution containing micro particles using a liquid bridge. (a) - (c) particle wires constructed from triangular lattice (close-packed structure) and (d) - (e) a close-packed 3D structure.

Figure 3 shows particle wires and 3D structures fabricated from ethanol solution containing polystyrene particles. The ethanol at the liquid bridge evaporated in about 1 min to form a particle wire, and droplets at the two ends evaporated in about 20 min. The liquid bridge of ethanol evaporated faster than that of water for several reasons. The saturated vapor pressure of ethanol (59 mmHg (0.078 atm) at 25 °C) is higher than that of water (24 mmHg (0.031 atm) at 25 °C), explaining the difference in the evaporation rate of the two droplets. The ratio in evaporation rate of the ethanol liquid bridge to the ethanol droplets is higher than that of the water liquid bridge to the water droplets. This can be explained as follows: Water has high surface tension (71.8×10^{-3} N/m at 25 °C) compared with ethanol (22.0×10^{-3} N/m at 25 °C). Ethanol existed along patterned hydrophilic regions with small meniscus at the angle between

droplets and a liquid bridge. However, water formed large meniscus at the angle between droplets and a liquid bridge, causing a wide line width of water liquid bridge compared with ethanol on our patterned surfaces. Additionally, the water liquid bridge was higher than that of ethanol due to high surface tension. These made the cross-section area of water larger than that of ethanol. The thick liquid bridge evaporated slowly because of its large volume and low vapor pressure calculated from the Kelvin equation in which the smaller convex liquid surface gives rise to higher internal pressure and faster evaporation rate¹. Furthermore, the solution at the droplets flowed into a liquid bridge and this further complicated the evaporation mechanism.

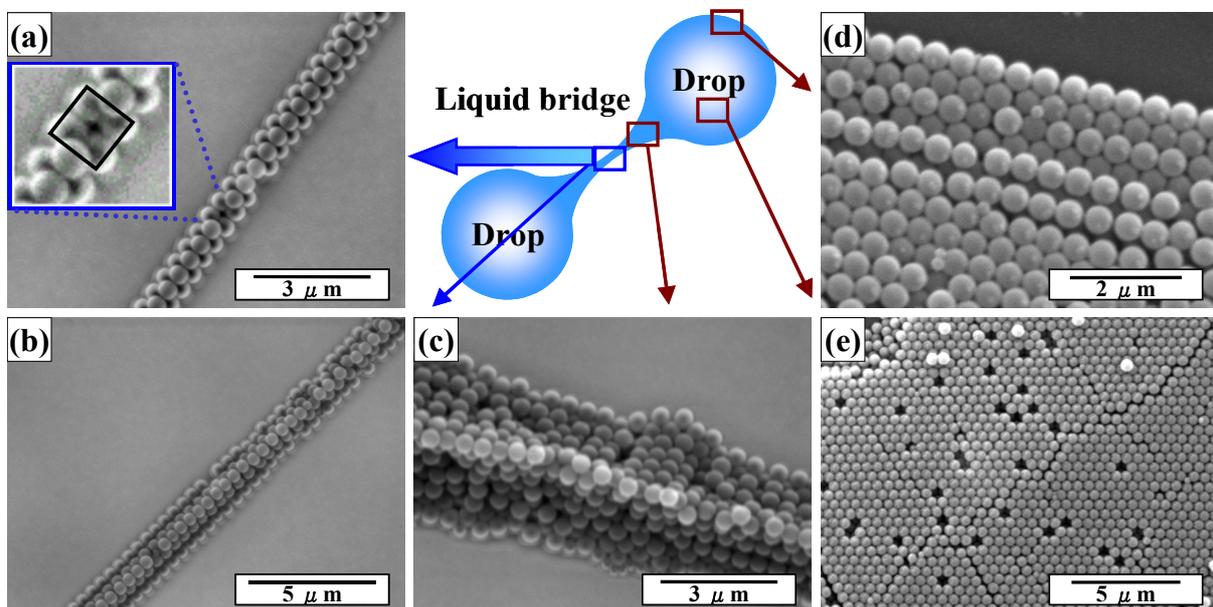


Figure 3. SEM micrographs of particle structures fabricated from ethanol solution containing micro particles using a liquid bridge. (a), (b) particle wires constructed from square lattice, (c) particles deposited on edge of silanol line and (d), (e) close-packed 3D structures.

A narrow particle wire was formed at the center of the liquid bridge (Fig. 3a, b), and wide wires were formed at the edges of the liquid bridge (Fig. 3c) along the silanol line. The particle wire in Fig. 3a is not a close-packed structure and is constructed from a square lattice, which is a metastable phase compared with a close-packed structure. High dispersibility of particles is necessary to form a close-packed structure in the solution. However, the particles dispersed well in ethanol and the dispersibility of particles in ethanol is similar to that in water. This shows that the non-close-packed structure was caused not only by the influence of

dispersibility but also by many other factors. Movement and rearrangement of deposited particles is necessary to construct a close-packed structure. However, the ethanol evaporated quickly and suppressed the movement of particles by liquid bridge force. Additionally, adhesion between particles and a substrate, and cohesion between particles probably caused moderate suppression of the rearrangement of particles. Factors such as evaporation rate, interaction force between particles, and interaction force between particles and a substrate were important in the packing process. Close-packed 3D structures were also formed on large silanol regions (Fig. 3d, e), and they contained many defects (Fig. 3e). The ethanol evaporated so quickly that the particles did not rearrange well to form a close-packed structure during evaporation of ethanol. This is one of the factors of forming a loosely packed structure. To directly evaluate the effect of the evaporation rate, a similar experiment using ethanol was conducted in a small airtight container with small pinholes to allow the ethanol to evaporate slowly. The size and number of pin holes were adjusted for ethanol at the liquid bridge to evaporate in about 24 h. The particle wire constructed from a close-packed structure was formed after about 24 h, and droplets at both ends were dried after about 48 h. The close-packed 3D structures were formed in large silanol regions. The number of defects was smaller than that formed from the ethanol solution with a shorter time and was similar to that formed from water. The humidity in the container was close to 100 % and the saturated vapor pressure of ethanol was 59 mmHg (0.078 atm) at 25 °C. This showed that particles dispersed well in ethanol and the interaction between particles and a substrate was sufficiently weak to produce a close-packed structure in the drying process of 24 h. Additionally, the results showed that not only the interaction force between particles and that between particles and a substrate, but also the evaporation rate needs to be controlled to fabricate particle wires.

Accuracy of particle arrangement was evaluated from Fig. 3(a) as calculated in recent work². The center position $((x_i, y_i) \mu\text{m})$ of each particle in an upper layer was plotted to estimate the standard deviation. The bottom left corner of Fig. 3(a) was set to be the origin of the x-y coordinate.

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

$$f(x) = 1.3965x - 5.3344, \quad (1)$$

$$\cos \theta = 0.5822, \quad (2)$$

Standard deviation from the approximated straight line is described by the expression,

$$\left[\sum_i \{\cos \theta \cdot (f(x_i) - y_i)\}^2 \right]^{1/2}$$

$$S \text{ (standard deviation)} = \frac{\quad}{n-1}, \quad (3)$$

where n is the number of particles ($n = 19$). The accuracy of the particle arrangement in Fig. 3(a) was estimated to be $S = 1.63 \times 10^{-3}$. This is lower than that of the particle arrangement obtained in our previous work².

Conclusions

We developed a novel process to fabricate particle wires on hydrophilic regions of a patterned SAM. Ethanol or water containing particles was separated into two droplets with a liquid bridge between the droplets along hydrophilic regions of a patterned SAM. Particle wires constructed from a close-packed structure or non-close-packed structure were then formed through self-assembly between two droplets after drying of the solution.

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4.7 Self-assembly fabrication for two-dimensional orderly array of particle wires

An orderly array of particle wires constructed from a close-packed structure was fabricated from colloidal solution. This process doesn't require the preparation of patterned templates and movement of liquid surface was used for assembly and patterning of particles.

Self-assembly fabrication for two-dimensional orderly array of particle wires.

The OTS-SAM was immersed into ethanol solution (80 ml) containing SiO₂ particles (1000 nmφ, 10 mg). The bottom of the solution was heated at 70°C and the condenser tube was kept at the top of solution to cool it. The temperature difference between the top and bottom of the solution was controlled so as to stir and move particles by convection. The surface of the solution was moved on the OTS-SAM surface by evaporation of ethanol. Particles began to assemble at the surface of the solution (Fig. 1(a)) and the particle layer was fabricated by the movement of solution surface (Fig. 1(b)). Further evaporation of solution caused separation of the particle layer and solution surface (Fig. 1(c)) because particles were not supplied sufficiently from the solution. The liquid surface was then dropped off and the particle layer was separated from the solution surface (Fig. 1(d)). The next particle layer was formed by the same procedure described above (Fig. 1(e)). Consequently, separated particle wires, i.e. an array of particle wires, were successfully fabricated by our newly developed method (Fig. 1(f), 2(a-d)).

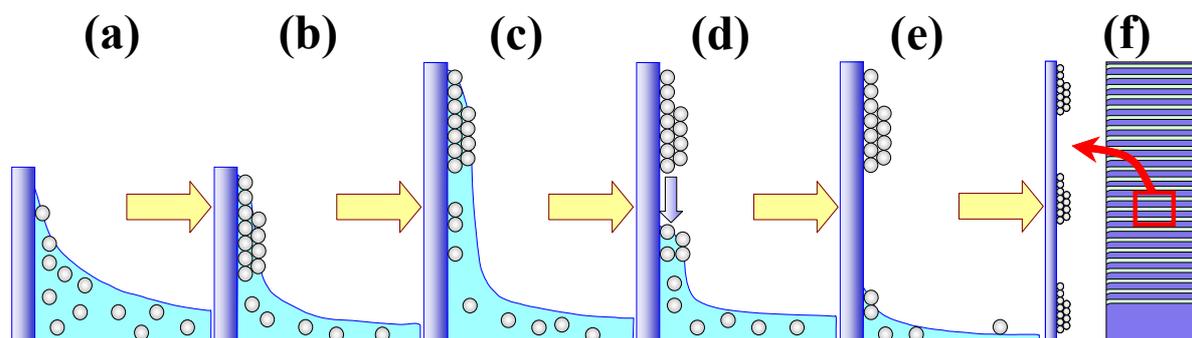


Figure 1. Schematic for self-assembly process to fabricate an orderly array of particle wires constructed from a close-packed structure. (a) beginning of particle arrangement, (b) separation of particle wire and liquid surface, (c) further separation, (d) drop off of solution surface, (e) arrangement of next particle wire, (f) array of particle wires.

After having been immersed in the solution which evaporates fast, the substrates were observed by a scanning electron microscope (SEM; S-3000N, Hitachi, Ltd.), an optical microscope (BX51WI Microscope, Olympus Optical Co., Ltd.) with a digital camera (DP50, 5.8 megapixels, Olympus Optical Co., Ltd.) and a computer for capturing data, and a digital video camera recorder (DCR-TRV 50, Sony Corporation) with optical magnifying glass. The width and interval of particle wires were shown to be about 150 μm and 200 μm , respectively (Fig. 2(a)). Particle wires were constructed from a close-packed particle structure and their upper side showed high feature edge acuity (Fig. 2(c)). Array of particles was finished suddenly as shown on the bottom side of particle wires (Fig. 2(d)). These observations suggested that particle wires were formed from the upper side and cut by drop-off of the solution, and are consistent with the procedure in Fig. 1. The mechanism of the assembly process and control of width, interval and thickness of particle wires are further discussed in a separate article.

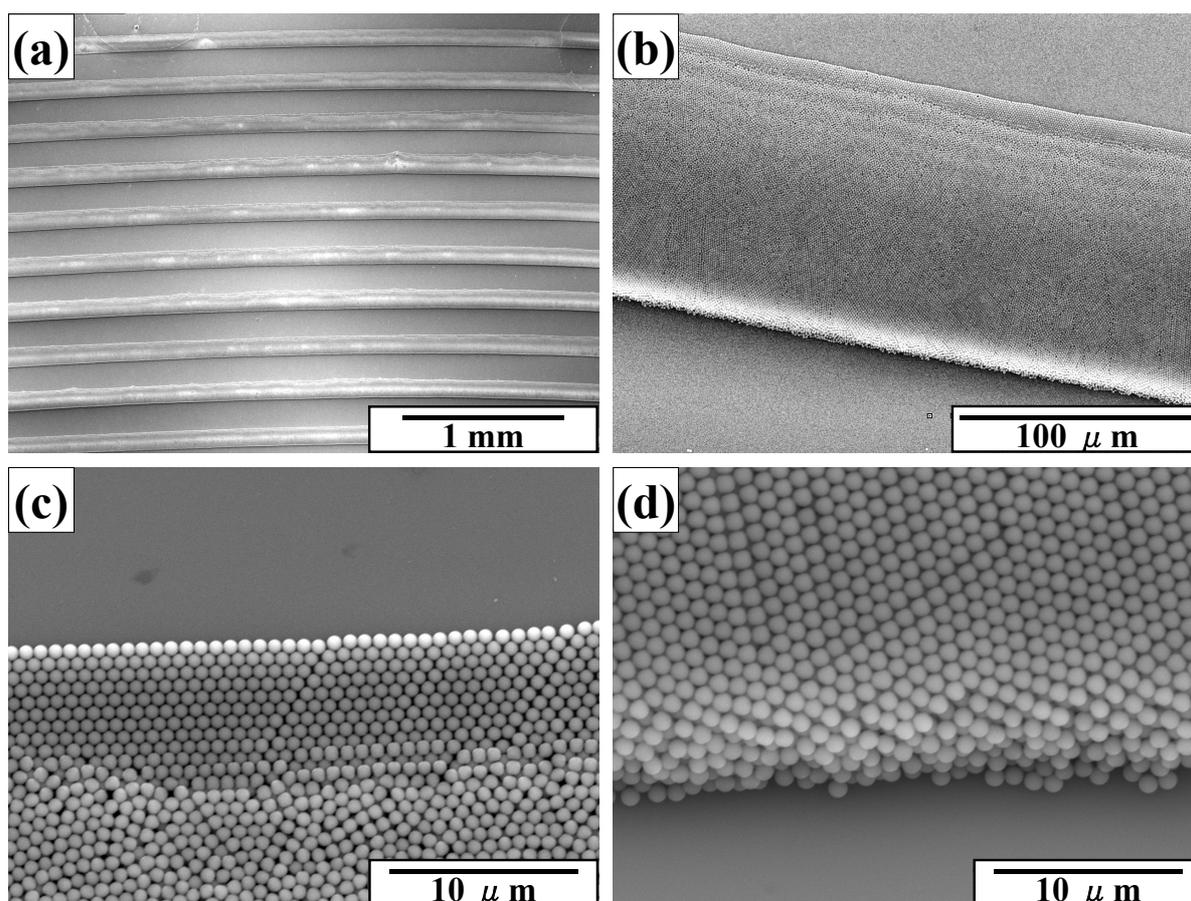


Figure 2. SEM micrographs of array of particle wires. (a) array of particle wires, (b) magnified particle wire, (c) upper side of (b), (d) bottom side of (b)

Particle wires showed iridescent diffraction (Fig. 3) caused from the high ordinality of the particle array shown in Fig. 2. Diffracted wave number was changed by diffraction angle. Additionally, particle wires were formed on the OTS-SAM from the ethanol solution (80 ml) containing a small amount of SiO₂ particles (1000 nm ϕ , 1 mg) to fabricate thin wires constructed from a mono-particle layer (Fig. 4). Particles were supplied to particle wires slowly from the solution. The number of particle layers was shown to be controlled by the change of particle number in the solution.

Furthermore, the particle layer was formed on the whole area of OTS-SAM by the use of water which evaporates slowly compared with ethanol. The particle layer was also formed on the whole area of OTS-SAM from ethanol solution sealed in an airtight container which has small holes to evaporate solution slowly. Drop-off of the solution was not observed and particles were supplied to the particle layer continuously. Fast movement of the solution surface caused by quick evaporation or lift of substrate is probably necessary to drop-off the solution surface which allows to fabricate separated particle wires.

Particles were not observed between particle wires formed on hydrophobic OTS-SAM (Figs. 2, 3). OTS-SAM repelled ethanol and extra particles were swept by the drop-off of the solution. On the other hand, many extra particles were observed between particle wires formed on a hydrophilic silicon substrate. Ethanol wetted completely to cover the silicon substrate thinly and leave particles between particle wires in their drying process. Wettability of substrate was shown to be important for removal of extra noise particles.

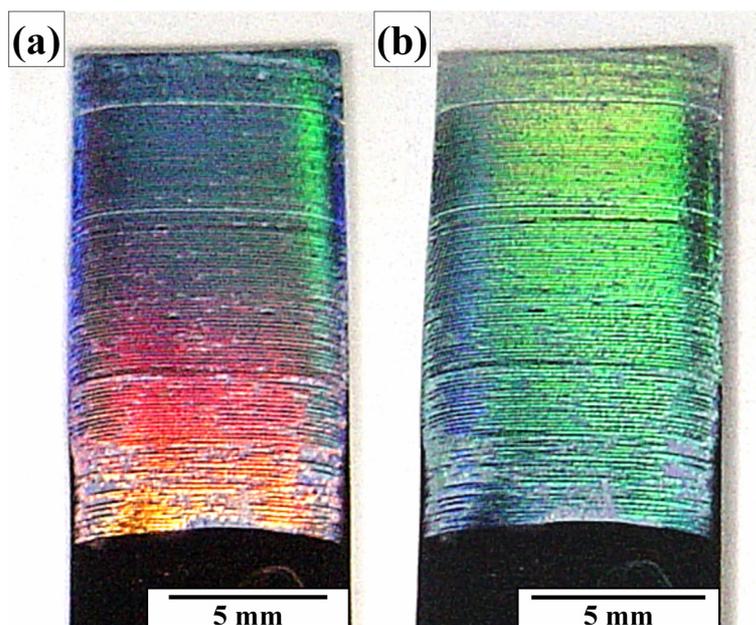


Figure 3. Photographs of particle wires; (a) front shot and (b) cross shot.

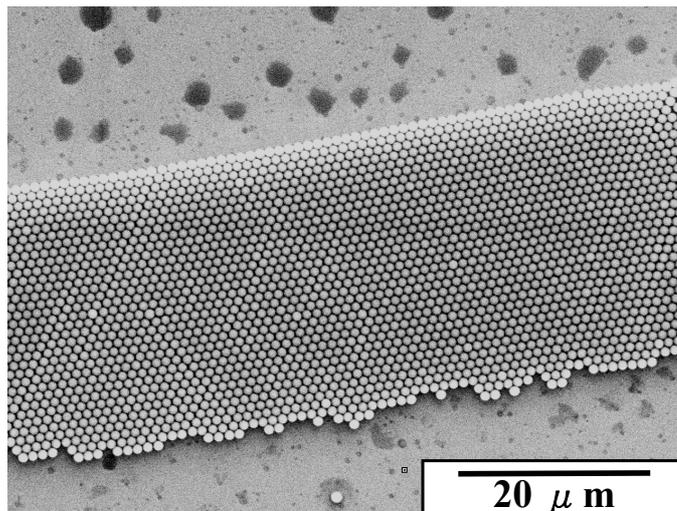


Figure 4. SEM micrograph of a particle wire constructed from a monolayer of particles.

Conclusions

In summary, we have proposed a novel process to fabricate separated particle wires self-assembly and realized particle wires constructed from a close-packed multi-particle layer or mono-particle layer on OTS-SAM from ethanol solution. The mechanism of this process will be discussed in a separate article, and this process should be improved to fabricate desired nano/micro-patterns of particle assembly.