Patterning of Silica Particles Using Self-Assembly on Two-Dimensional Patterns Fabricated from Phase-Separated Langmuir-Blodgett Films

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In this study, self-assembled arrays of silica particles were formed on the two-dimensional patterns of the functionalized templates fabricated from phase-separated mixed Langmuir-Blodgett films. Immersion of the functionalized templates into silica particle dispersion led to the formation of silica particle arrays due to the electrostatic interaction between the dissociated carboxylic groups originating from bovine serum albumin on the silica particles and the amino groups on the functionalized templates.

Key words: Self-assembled array, Langmuir-Blodgett film, Phase-separated structure

1. INTRODUCTION
Nanoparticles show the size-dependent unique properties which are applicable for chemical sensors [1], biosensors [2,3], optical [4,5] and electronic devices [6] by the control of their arrangements. Scanning with probes [7,8] and irradiation with laser [9,10] have been used as external stimuli to fabricate nanoparticle arrays. However, these techniques require complicated processes and/or elaborate skills to manipulate particles. In contrast, the bottom-up method using spontaneous growth has also been investigated. This method uses gravitational force [11,12] and lateral capillary force [13]. Patterning of nanoparticles using conventional processes is difficult because the nanoparticle arrays are formed uniformly on the substrates.

The Langmuir-Blodgett (LB) technique is one of the promising bottom-up technologies to fabricate ultrathin films with well-defined structures. Phase separation often occurs in mixed LB films. We have shown that disk domains at the micrometer length scale and wire domains at nanometer length scale form in the phase-separated mixed LB films of fatty acid, silane coupling agent and hybrid carboxylic acid having both hydrogenated and perfluorinated alkyl moiety [14]. In addition, we have also succeeded in the fabrication of functionalized templates, the patterns of which reflect the phase-separated structures of three-component mixed LB films, by heat treatment, followed by selective removal of the conventional amphiphiles and immobilization of another silane coupling agent having a terminal functional group [14,15,16,17,18]. This study aims at the fabrication of self-assembled arrays of silica particles by a very simple procedure of immersing the functionalized templates in silica particle dispersion. Furthermore, the effect of the solvent of dispersion on the self-assembly of silica particles on the functionalized templates was also investigated.

2. EXPERIMENTAL SECTION
Eicosanoic acid (CH3(CH2)18COOH: H19A; Acros Organics) and (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (CF3(CF2)7(CH2)2SiCl3: F8H2SiCl; Gelest) were used as amphiphilic molecules for the preparation of LB films. The numbers following “H” and “F” denote the hydrocarbon and perfluorocarbon chain length, respectively. N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDA-Si; Gelest) was used to functionalize the templates. Hexane used as the spreading solvent was purchased from Dojindo.

A spreading solution at a concentration of 1.0 mM was spread on an aqueous subphase at 293 K. The molar ratio of H19A to F8H2SiCl was 1 : 9. Molecules were compressed at 1.2 × 10^-2 nm^2/molecule · min after the evaporation of the spreading solvent. The Langmuir film was transferred at 10 mN/m using the vertical dipping method at a withdrawal speed of 5 mm/min onto Si wafers with oxidized surfaces. The Si wafers were kept in aqueous NH4OH and H2O2 at 371 K for 10 min and rinsed with water before use.

The phase-separated LB films were subjected
to the heat treatment at 383 K for 30 min, followed by ultrasonication in ethanol for 5 min, to fabricate templates. The templates were immersed in 10 mM EDA-Si methanol solution for functionalization. Silica particles (sicastar) whose surface is modified with carboxylic groups originating from bovine serum albumin (BSA) were purchased from micromod partikel technologie. The particle size was 70 nm. The concentration of sicastar dispersion was 25 mg/ml. This dispersion was diluted with pure water to prepare silica particle dispersion for the fabrication of silica arrays on the functionalized templates unless otherwise stated. The volume ratio of undiluted dispersion : pure water was 1 : 9. In addition, undiluted silica particle dispersion was also diluted with acetic acid or ammonia to investigate the effect of pH on the formation of silica particle arrays. The volume ratio of (undiluted dispersion) : (pure water) : (acetic acid or ammonia) was 1 : 4.5 : 4.5. The pH values of the dispersion were 2 and 13 for solutions of acetic acid and ammonia, respectively. The functionalized templates were immersed into the diluted silica particle dispersion at room temperature for 60 min.

3. RESULTS AND DISCUSSION

Figure 1(a) shows an AFM image of a phase-separated mixed LB film. The AFM image shows the presence of disk domains of the size of 1-5 µm. The domain region is higher than the rest of the surface by about 1 nm. This demonstrates that the ex-domain region and the rest of the surface are formed by H19A and F8H2SiCl, respectively. Figure 1(b) shows the AFM image of the LB film after the heat treatment at 383 K and the ultrasonication in ethanol. The ex-domain region is lower than the surrounding region. This indicates the formation of covalent bond between F8H2SiCl and the substrate by the heat treatment and the selective removed of H19A by the ultrasonication. The surface of the resultant template has silanol groups confined in the

ex-domain region that are surrounded by the self-assembled monolayer (SAM) of F8H2SiCl. The surface silanol groups present in the ex-domain were reacted with EDA-Si for the functionalization of the templates with amino groups (Figure 1(c)).

Figure 2(a) shows the AFM image of a functionalized template after immersing into the diluted silica particle dispersion. It is evident that the silica particles adsorb selectively on the disk domain region. This demonstrates that the self-assembled arrays of silica particles form on the two-dimensional patterns of the functionalized templates.

Next, we investigated the effect of the amino groups in the ex-domain region on the arrangement of silica particles using templates without functionalization. The ex-domain regions of the unfunctionalized templates are covered with silanol groups of Si wafers. Figure 2(b) shows an AFM image of a template after the immersion into the diluted silica particle dispersion. It is evident that the silica particles do not adsorb on either the ex-domain region or the rest of the surface. This clearly shows that the formation of self-assembled arrays of silica particles requires the presence of amino groups on the surface.

Finally, we investigated the effect of pH on the self-assembled arrays of silica particles. Figure 3 shows the AFM images of functionalized templates after immersion into the diluted silica particle dispersion with adjusted pH values.
When functionalized templates were immersed into the acidic dispersion, the silica particles adsorbed on both the ex-domain region and the rest of the surface (Figure 3(a)). Figure 3(b) shows an AFM image of the functionalized template after immersion into basic silica particle dispersion. It is evident that the silica particles do not adsorb on the functionalized templates under the present conditions. These results indicate that the value of pH strongly affects the formation of self-assembled arrays of silica particles.

Above results are explained by considering mainly the local zeta potential of functionalized and unfunctionalized templates and in one case the interfacial tension of the templates [19,20]. Figure 4 shows the schematic illustrations of the formation of self-assembled arrays of silica particles under the various conditions investigated above. First, the formation mechanism of self-assembled arrays using functionalized and unfunctionalized templates is discussed. The pH value of the diluted silica dispersion is about 6 because pure water is used for the dilution. The surface of silica particles modified with BSA is negatively charged in the dispersion due to the dissociation of carboxylic groups. Amino groups in the ex-domain region of the functionalized templates are positively charged at around pH = 6. The rest of the surface of the functionalized templates is covered with trifluoromethyl groups and is negatively charged. Electrostatic attractive force between the silica particles and the amino groups results in the formation of the self-assembled arrays of silica particles.

Electrostatic repulsive force between the surface of silica particles and the amino groups in the ex-domain region of the functionalized templates are positively charged at around pH = 6. The rest of the surface of the functionalized templates is covered with trifluoromethyl groups and is negatively charged. Electrostatic attractive force between the amino groups and the surface of the functionalized templates results in the absence of silica particle adsorption as shown in Figure 4(b).

Next, the effect of pH on the formation of self-assembled arrays of silica particles is discussed. Figure 4(c) shows the schematic illustration of the behavior of the silica particles at pH = 2. The ex-domain region and the rest of the surface on the functionalized templates are positively and negatively charged, respectively. The amount of dissociated carboxylic groups on the silica surface at around pH = 2 is much smaller than that around at pH = 6. Still, the driving force of the adsorption of the silica particles in the ex-domain region should be electrostatic attractive force between the amino groups and the surface of the silica particles. In contrast, we should consider the interfacial tension to explain that the silica particles adsorb on the rest of the surface of the functionalized templates. We should consider three types of interfacial tension involved in the adsorption of the silica particles:

1. The interfacial tension \( \gamma_{fs} \) between the surface of trifluoromethyl groups and the silica particles covered with carboxyl groups and carboxylate anions.
2. The interfacial tension \( \gamma_{fw} \) between the surface of trifluoromethyl groups and water.
3. The interfacial tension \( \gamma_{sw} \) between the silica particles and water. The inequality \( \gamma_{fw} + \gamma_{sw} > \gamma_{fs} \) holds because the surface of trifluoromethyl groups has water-repellent properties. The energy gain should be larger than the electrostatic interaction due to the fact that only a small amount of carboxylate anions is present on the surface of the silica particles at this pH.

The silica particles are negatively charged at around pH = 13 with a larger amount of carboxylate anions than that at around pH = 6. Both the ex-domain region and the rest of the surface are negatively charged at this pH, which results in the absence of the silica particle adsorption.

4. CONCLUSIONS

In this study, we have prepared the self-assembled arrays of silica particles on the two-dimensional patterns of the functionalized templates fabricated from phase-separated mixed LB films. The electrostatic interaction between the carboxylic groups of the silica particles and the amino groups on the functionalized templates leads to the selective adsorption and the arrangement of silica particles. The present study provides us with a means to fabricate arrays of various inorganic materials by adjusting zeta potentials of inorganic particles and silane coupling agents introduced into the ex-domain region. This technique will be important in the fabrication of patterned arrays of inorganic nanoparticles for the applications to sensors, photonic materials, optoelectronic materials and catalysts.
REFERENCES


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