Nanowire Formation in Two-component-mixed Langmuir–Blodgett Films of Fatty Acid and Silane-coupling Agent

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We have found the formation of nanowires in two-component-mixed Langmuir–Blodgett (LB) films of fatty acid and silane-coupling agent for the first time. The phase-separated structures of the mixed LB films were controlled by adjusting intermolecular interactions. The size and shape of the domains were explained by considering two competing interactions of line tension and dipole–dipole interaction.

Self-assembly enables us to control structures of organic and inorganic materials at the nanometer and micrometer length scales.[1–8] Because of the availability of molecular design to control intermolecular interaction, self-assembly of organic materials has been extensively investigated. Lateral patterning of organic materials has been performed using both top-down[8] and bottom-up[1–7] methods to confine materials in a designed manner. We focus on lateral patterning using bottom-up methods. Microphase separation has been used to form patterns of block copolymers.[6] We have reported that phase separation at the nanometer length scale occurs in two-component-mixed Langmuir–Blodgett (LB) films of fatty acid and hybrid carboxylic acid.[5] The size and shape of the domains can be controlled by adjusting intermolecular interaction. Fabrication of templates is necessary to pattern functional materials using phase-separated LB films. For that purpose, silane-coupling agent having a perfluoroalkyl chain is mixed as a third component that can form covalent bond with the solid substrates. Selective removal of fatty acid and hybrid carboxylic acid gives templates to confine organic and inorganic materials at the nanometer length scale.[5] The problem of using three-component LB films for the fabrication of templates is the possibility that hybrid carboxylic acid is dissolved in the region of silane-coupling agent owing to the similarity of the hydrophobic moieties, which blurs the boundaries of confined materials. To solve this problem, one of the strategies is to use two-component-mixed LB films of fatty acid and silane-coupling agent. However, the formation of circular domains at the micrometer length scale has been reported in mixed LB films of fatty acid and silane-coupling agent.[1,4]

In this paper, we report the successful fabrication of nanowires in two-component-mixed LB films of fatty acid and silane-coupling agent by adjusting intermolecular interaction.

We used fatty acid $C_mH_{2m+1}COOH$ ($m = 15–21$, abbreviated as HmA) and silane-coupling agent $C_nF_{2n+1}C_2H_4SiX_3$ ($n = 4–12$, X = Cl, OCH$_3$, and OC$_2$H$_5$: abbreviated as FnH2SiX). FnH2SiX ($n = 4, 6, 10,$ and 12) was synthesized according to the literature.[9] Other materials were purchased and used as received. Monolayer measurements were performed on a Lauda film balance. Molecules were dissolved in hexane under a dry N$_2$ atmosphere, spread and compressed on pure water at temperatures of 10–30 °C. Monolayers were transferred onto Si-wafers

using the vertical dipping method at a surface pressure of 10 mN m^{-1}. AFM observations were performed using a Seiko SPA300 microscope in a dynamic force mode with a Si cantilever.

Figure 1 shows surface pressure–area isotherms of FnH2SiCl at 30 °C. FnH2SiCl having a short alky chain ($n = 4$ and 6) shows an onset point of surface pressure at a very small area, indicating the lack in the ability of forming monolayers owing to the insufficient length of the perfluorocarbon. The surface pressure of FnH2SiCl having a longer alky chain ($n \geq 8$) rises at area per molecule larger than 0.20 nm^2, suggesting the monolayer formation considering that the cross section of a perfluorocarbon is ca. 0.25 nm^2.[10] FnH2SiOCH$_3$ and FnH2SiOC$_2$H$_5$ showed onset points of surface pressure at 30 °C much smaller than those of FnH2SiCl ($n \geq 8$).

Figure 2 shows the AFM images of single-layer mixed LB films of F8H2SiCl and HmA ($m = 15$ and 17) at a molar ratio of 1 to 1 fabricated at 20 °C. Nanowires form in the mixed LB film of F8H2SiCl and H15A with a height difference of less than 0.5 nm, whereas circular domains form in the mixed LB film of F8H2SiCl and H17A with a height difference of ca. 1 nm. Circular domains were also found in mixed LB films of F8H2SiCl and HmA ($m = 19$ and 21).

Figure 3 shows the AFM image of a single-layer mixed LB film of F10H2SiCl and H17A at a molar ratio of 1 to 1 fabricated at 20 °C. Nanowires form with a height difference of 0.5–1.0 nm. The width of nanowires is several tens of nanometers, much smaller than that in the mixed LB films of F8H2SiCl and H15A. In mixed LB films of F10H2SiCl and H19A at a molar ratio of 1 to 1, nanowires with a width of several hundreds of nanometers formed. Nanowires in the mixed LB film F10H2SiCl
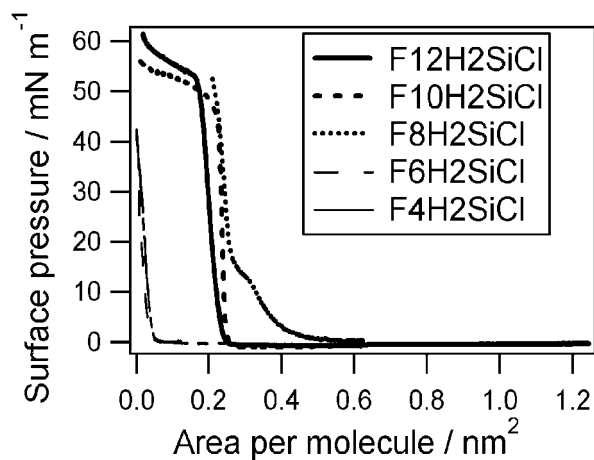
Figure 1. Surface pressure–area isotherms of FnH2SiCl at 30 °C ($n = 4, 6, 8, 10,$ and 12).
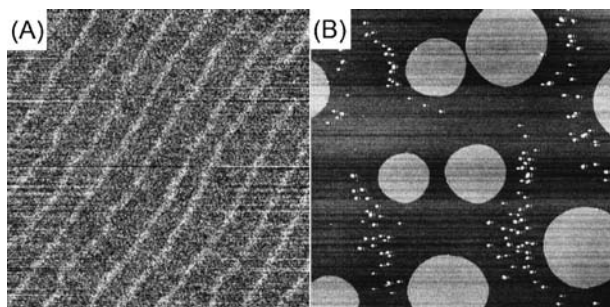
Figure 2. AFM images of single-layer mixed LB films of F8H2SiCl and HmA at a molar ratio of 1 to 1 fabricated at 20 °C. (A) $m = 15$, scanned area is 5 µm × 5 µm, (B) $m = 17$, scanned area is 20 µm × 20 µm.
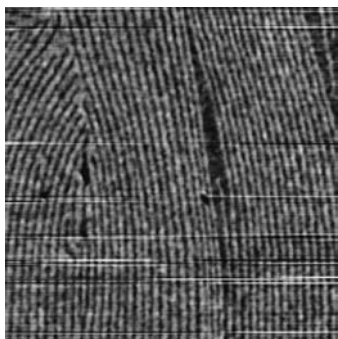

Figure 3. AFM image of a single-layer mixed LB film of F10H2SiCl and H17A at a molar ratio of 1 to 1 fabricated at 20 °C. Scanned area is 2.5 µm × 2.5 µm.

and H17A are better-defined than those in the LB film of F8H2SiCl and H15A because the stabilizing energy between the alkyl chains increases with an increase in alkyl chain. Further, nanowires in the mixed LB film of F10H2SiCl and H17A are better-defined than those in the three-component LB films[5] probably because of the absence of hybrid carboxylic acid in the present study.

Above results are explained by considering the contributions of line tension and dipole–dipole interaction to the size and shape of the domains in the mixed LB films.[11] Line tension represents free energy necessary to create a unit length of domain boundary and favors the formation of large and/or circular domains. Dipole–dipole interaction in the Langmuir and LB films is repulsive because of the ordered arrangement of molecules in the films. Dipoles that are effective in the mixed films are those positioned at both ends of the molecules. This interaction favors the formation of small and/or elongated domains.

We consider the effect of the lengths of both the alkyl chain of HmA and the perfluoroalkyl chain of FnH2SiCl on the two competing interactions. Line tension should be proportional to the difference between the homo and the hetero interactions, with the former being the interaction between the same chemical species and the latter between different chemical species, respectively. With an increase in m, the homo interaction decreases due to the increased stabilizing energy arising from the dispersive interaction between the alkyl chains of HmA. In contrast, the hetero interaction remains almost constant because HmA forms

higher regions in the mixed LB films. In total, line tension increases with an increase in m, which agrees with the results in Figure 2 and those for the LB films with $n = 10$ and $m = 17$ and 19. The increase in n decreases both the homo and the hetero interactions. The homo interaction decreases owing to the decrease in dispersive interaction between the perfluoroalkyl chains of FnH2SiCl. The hetero interaction also decreases because of the decrease in dispersive interaction between the alkyl chain of HmA and the perfluoroalkyl chain of FnH2SiCl. Line tension decreases with an increase in n because the decrease in the latter is much larger than that in the former[12] and that in the latter contributes twice as much as the former. This is also consistent with the present results in that the size of the domains decreases with an increase in n.

We consider the dipole–dipole interaction within the domains because that is dominant in the nanostructure formation. Dipoles at both ends of the molecules form two layers of dipoles. The interaction of the dipoles within the same layer does not depend on the value m or n. The interaction between the dipoles positioned in the different layers does not depend on the value m or n either, considering that a layer of dipoles should produce a constant electric field over a very small distance of several nanometers if the boundary effect is neglected.

This study demonstrates for the first time that nanowires can be fabricated in two-component-mixed LB films of fatty acid and silane-coupling agent by adjusting intermolecular interactions. By increasing the length of perfluorocarbon of FnH2SiCl, longer fatty acid can be used to form nanowires, resulting in the formation of well-defined nanowires. Further, the nanowires are better-defined than those in three-component-mixed LB films containing hybrid carboxylic acid. Further study is now in progress to control the phase-separated structures of two-component-mixed LB films more precisely and to fabricate templates using the mixed LB films for the confinement of functional materials.

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