Surfactant Templates

Dramatic Shape Modulation of Surfactant/Diacetylene Microstructures at the Air–Water Interface

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Abstract: Langmuir monolayers constitute a powerful platform for self-assembly and organization of amphiphilic molecules. Controlling the structural features of condensed domains formed within Langmuir monolayers, however, is a challenging task. The formation of remarkably diverse condensed microstructures is demonstrated in binary monolayers comprising of a surfactant (octadecylmelamine) and a diacetylene monomer. The mole ratio between the two constituents and composition of the aqueous subphases (specifically pH and which dissolved metal ions are present) dramatically modulated the shapes and dimensions of microstructures formed at the air–water interface. The self-assembled microstructures could be transferred from the water surface onto solid substrates, and subsequently further served as templates for gold coating, yielding electrically conductive microwires.

Introduction

The design and assembly of two-dimensional (that is, surface) patterns are core objectives in diverse technologies, including microelectronics, sensing, microfluidic devices, and others. While most micro- and nanoscale patterns for practical applications and devices are currently fabricated by "top-down" lithography methods, "bottom-up" approaches have emerged as promising alternatives for generation of organized patterns. Bottom-up techniques generally rely upon molecular self-assembly phenomena to produce spatially defined structures. In this context, Langmuir monolayers are considered a promising platform for generation of organized two-dimensional structures and patterns.

Varied experimental parameters enable modulation of structural features and organization of Langmuir monolayers. Numerous studies have analyzed the effects of temperature, molecular properties of monolayer constituents, and subphase composition upon the structure and organization of monolayers at the air–water interface. Inclusion of different solutes or metal ions into the aqueous subphase, in particular, are known to affect monolayer properties. However, assembly and controlled modulation of condensed domains within Langmuir monolayers, which could be further transferred from the water surface onto solid supports, are still considered a challenging task. Multi-component monolayers, in particular, have been shown to promote formation of organized condensed domains through phase segregation between the two (or more) amphiphilic molecules comprising the monolayers.

We demonstrate the assembly of remarkably diverse condensed microstructures in binary Langmuir monolayers comprising a surfactant molecule, octadecylmelamine (OM), and a diacetylene monomer, N-(2-aminomethyl)tricosa-10,12-diyname (TEA). OM has been previously shown to display interesting self-assembled structures at the air–water interface. Diacetylene Langmuir monolayers (and monolayers comprising polymerized diacylenes, or polydiacetylenes) have been widely studied, adopting diverse structures at the air–water interface and exploited as platforms for sensing applications. Binary monolayers of diacylenes and lipids have been shown to exhibit interesting thermodynamic and structural properties, producing both interspersed mixed domains as well as segregated monolayer morphologies.

This study explores the effects of the mole ratio between OM and TEA in the binary monolayers and subphase composition upon structural properties and monolayer organization. Surprisingly, we recorded a remarkable structural variety of condensed domains assembled upon compression of the mixed monolayers in the different conditions examined. Specifically, through modulating the monolayer compositions, subphase pH, and metal ions in the subphase, we generated a variety of microstructures, including rods, flowers, disks, fibers, and foam-like structures. The condensed microstructures could be transferred from the water surface onto solid substrates, and were further utilized as templates for deposition of conductive gold patterns.

Results and Discussion

Microstructure assembly and in situ characterization

Figure 1 presents an overview of microstructure formation within N-(2-aminomethyl)tricosa-10,12-diyname (TEA)/octadecylmelamine (OM) mixtures at the air–water interface. Specifi-
cally, condensed domains were formed after isothermal compression of Langmuir TEA/OM monolayers at different mole ratios, as well as placed over aqueous subphases having different ion compositions. Remarkably, as summarized in Figure 1, diverse shapes and dimensions of microstructures were observed, of which the structural properties were dependent upon the mole ratio between the two amphiphilic molecules and the presence of different metal ions within the aqueous subphase.

Figures 2–4 present thermodynamic and structural characterization of the OM/TEA Langmuir monolayers. The compression isotherms and Brewster angle microscopy (BAM) analysis presented in Figure 2 underscore the effect of mixing the two amphiphiles within the Langmuir monolayers. Compression isotherms of the monolayers comprising the individual surfactants indicate a condensed monolayer for pure OM (Figure 2 A i) and a more fluid monolayer in case of TEA, typical for diacetylene systems (Figure 2 A ii).\[16\] The limiting molecular area of OM, extrapolated from the linear portion of the $\pi$–$A$ isotherm to the zero surface pressure (Figure 2 A i), is approximately 0.21 nm$^2$/molecule, which is smaller than TEA (around 0.52 nm$^2$/molecule) and ascribed to the conjugated plane of OM.\[26\]

The compression isotherms recorded for the mixed monolayers, OM/TEA (mole ratio 1:2; Figure 2 A iii) OM/TEA (1:4; Figure 2 A iv), and OM/TEA (1:6; Figure 2 A v), appear as intermediates between the two pure monolayers, consistent with interpenetration of the two components. Notably, the overall shapes of the isotherms recorded for the two mixtures trace the isotherm of pure TEA, indicating greater effect of the diacetylene upon monolayer fluidity, possibly related to its higher concentration.

The BAM images in Figure 2B illuminate the surface organization of the Langmuir monolayers. The BAM data reveal a significant difference between the uniform condensed OM monolayer giving rise to a bright, reflective film (Figure 2 B i), and the TEA monolayer, which is comprised of elongated condensed domains spread over the water subphase (Figure 2 B ii). The BAM images recorded for the mixed monolayers display abundant “rod-shaped” structures for the 1:2 and 1:4 mole ratios between OM and TEA (Figure 2 B iii, iv), and more spherical domains in the monolayer exhibiting 1:6 ratio (Figure 2 B v). The BAM results of the mixed Langmuir monolayers confirm the occurrence of effective mixing between the two molecular constituents, giving rise to distinct monolayer organization. Notably, the BAM data also echo the thermodynamic analysis in Figure 2A indicating a more pronounced contribution of the TEA component within the mixed films, leading to the emergence of condensed domains in all mole ratios examined.

While Figure 2 illuminates the organization of mixed OM/TEA monolayers at the air–water interface, an important focus of this work concerns the consequences of modulating subphase composition upon film organization and microstructure formation. The aqueous subphase is expected to intimate affect film properties since the hydrophilic head-groups of amphiphilic constituents of Langmuir monolayers (such as OM and TEA in this study) are immersed in the aqueous subphase and interact with ionic and polar species in solution.\[16, 27\] Indeed, Figures 3 and 4 highlight the dramatic impact upon monolayer organization of modulating the pH of the subphase (Figure 3) or addition of different metal ions (Figure 4).

Figure 3 illustrates dramatic monolayer reorganization induced by altering the pH of the aqueous subphase. No dis-
creet domains were detected in the OM/TEA (1:2) monolayer deposited upon a subphase at pH 2 and compressed to 30 mN m⁻¹ (Figure 3 A). This result might be ascribed to protonation of the amino groups of the two amphiphiles which inhibits attraction and domain formation. Abundant circularly shaped domains, however, appeared in the monolayer upon raising the pH of the subphase to 4 (Figure 3 B), reflecting the formation of condensed domains that are most likely stabilized through hydrogen bonding among the partly protonated amphiphiles. Indeed, at pH > 6.5, the BAM experiment reveals ubiquitous aligned fiber-like domains assembled at the air–water interface, which are most likely formed through hydrogen bond network within the head-groups of the two amphiphiles. The prominent role of hydrogen bonding in thin film organization of diacetylenes and surfactants has been reported.[25, 28, 29]

Figure 4 demonstrates the dramatic structural effects recorded when different metal ions were added to the aqueous subphase prior to compression of the OM/TEA (1:2) monolayer at pH 6.5 (metal ion concentration in all experiments was 0.01 mM). Importantly, the structures shown in Figure 4 were formed through slow compression of the monolayers to 25 mN m⁻¹, thus likely correspond to equilibrium domain structures. The BAM image in Figure 4 B underlies no significant difference in the microstructural features compared to pure water (Figure 4 A) when the monovalent alkaline ions Na⁺ and K⁺ or the divalent ions Ca²⁺ or Mg²⁺ were present in the aqueous subphase. However, uniform, elongated, and more sparsely dispersed OM/TEA domains were apparent when the subphase contained Zn²⁺ ions (Figure 4 C). Similar BAM results were recorded when other divalent transition-metal ions, such as Pb²⁺ and Fe²⁺, were added to the subphase (data not shown).

In contrast to the BAM images in Figure 4 A–C which display elongated domains formed in the presence of alkali-metal, alkaline-earth, or divalent transition-metal ions, significantly different morphologies were observed when other metal ions were present in the aqueous subphase. Remarkable flower-shaped domains were apparent when trivalent Fe³⁺ ions were added to the subphase (Figure 4 D). In comparison, abundant small “disk-like” domains were detected when the subphase contained Ag⁺ ions (Figure 4 E). A similar configuration was recorded in the presence of another noble metal ion, namely Au³⁺, although in this case the condensed domains appeared fused together, forming a continuous foam-like structure (Figure 4 F).

The BAM data in Figure 4 attest to the close relationship between the ionic species in the subphase and microstructures formed upon compression within the mixed OM/TEA Langmuir monolayers. Corroborating the interpretation of the pH-induced monolayer reorganization in Figure 3, the experiments presented in Figure 4 point to strong interactions between ions and the head-group of the surfactants, which likely constitute the primary driving force for the self-assembly process at the air–water interface. Indeed, the distinct structural effects induced by specific metal ion types (that is, alkali, alkaline-earth, transition metals, high valency metals, and noble metals) supports a scenario in which interactions between the metal ions and nitrogen donors within OM and TEA significantly contribute to monolayer organization and particularly assembly of condensed mixed domains. Indeed, the monolayer organizations appear to be correlated to groupings of the ions tested, that is, monovalent ions, divalent ions, trivalent metal ions, and noble metals.
Ex-situ characterization

While the BAM analyses presented in Figures 2–4 demonstrate a remarkable variety subphase-modulated microstructures, a pertinent question is whether these assemblies can be transferred onto solid substrates, and thus could be potentially further utilized as building blocks for functional materials and practical applications. Accordingly, we transferred the compressed films shown in Figure 4 onto silicon surfaces using the horizontal transfer technique (Langmuir–Schaeffer), and examined the transferred films using atomic force microscopy (AFM, Figure 5). The representative AFM images in Figure 5 confirm that the microstructures formed at the air–water interface could be successfully transferred from the water surface without disrupting their unique structural features. Furthermore, the AFM analysis nicely reveals the fine morphological details of the microstructures. Specifically, the OM/TEA domains formed over a subphase containing Zn$^{2+}$ exhibit a remarkable hair-like structure (Figure 5 B), while an intricate dendritic shape is apparent when the subphase contained Ag$^+$ ions (Figure 5 D).

Applications

The AFM experiments depicted in Figure 5 indicate that the distinct microstructures assembled upon compression of the OM/TEA Langmuir monolayers can be transferred onto solid substrates. Accordingly, one can envision possible practical applications for the assembled microstructures. Figure 6 explores the use of the elongated microrods as templates for electrically conductive Au coating. In this experiment, we implemented a recently developed simple reaction process in which thin conductive Au layers are spontaneously formed upon incubation of [Au(SCN)$_4$]$^-$/C$_0$ with amine-displaying surfaces. [30] Specifically, we reacted the silicon-supported OM/TEA microstructures (which display amine moieties) with [Au(SCN)$_4$]$^-$ and subsequently examined their structural features and application as conduits for electrical current (Figure 6).

Figure 6 depicts scanning electron microscopy (SEM) images and an electrical conductivity profile of rod-shape domains grown above Zn$^{2+}$-containing subphase (Figure 4 C), transferred onto a silicon substrate and subsequently incubated within gold thiocyanate solution. Notably, the SEM image in Figure 6 A indicates that the rod morphology was retained after film transfer and Au deposition. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses confirm that a layer of metallic, crystalline gold formed upon the amine-containing microrods (Supporting Information, Figure S1). Figure 6 B depicts the conductivity measurements (Figure 6 B, left graph) and experimental setup (Figure 6 B, right image). Specifically, gold electrodes were pasted on the silicon surface after film transfer and Au coating of the microstructures. Microscopic examination of the surface subsequently enabled locating electrodes that were physically connected by the Au-coated micro-wires. Importantly, the linear appearance of the current–voltage ($I$–$V$) curve in Figure 6 B indicates an Ohmic behavior and confirms effective electron transport through the microrod.

Conclusion

We show that Langmuir monolayers comprising binary mixtures of a surfactant molecule (OM) and diacetylene derivative (TEA) produce condensed microstructures in remarkable structural diversity. Specifically, modulating the monolayer compositions (that is, the mole ratio between the two amphiphiles), subphase pH, and presence of metal ions in the subphase re-
sulted upon isothermal compression of the monolayers in appearance of rods, flowers, disks, fibers, and foam-like structures. The condensed microstructures could be transferred from the water surface onto solid substrates, and were further utilized as templates for deposition of conductive gold patterns. Overall, this study demonstrates that constructing surfactant/diacetylene Langmuir monolayers, combined with careful modulation of experimental parameters pertaining to monolayer properties and subphase composition, constitutes a vehicle for generating variety of condensed microstructures at the air–water interface that can be further utilized for practical usage.

**Experimental Section**

**Materials**

10,12-Tricosadiynoic acid (TrCDA) was purchased from Alfa Aesar. Zn(NO₃)₂, Pb(NO₃)₂, Ag(NO₃)₂, H[AuCl₄], FeCl₃, KCl, CaCl₂, MgCl₂, and FeCl₂ (all analytical reagents) were purchased from Sigma–Aldrich and used without further purification. 1,2-ethylenediamine, N-hydroxy succinimide (NHS), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), 2-chloro-4,6-diamino-1,3,5-triazine, octadecylamine, and anhydrous sodium hydrogencarbonate were purchased from Sigma–Aldrich and were used as received. The [Au(SCN)₄]⁺ complex was prepared according to previous reports. A solution of [H(AuCl₃)₂]H₂O in water (1 mL; 24 mg·mL⁻¹) was added to a solution of KSCN in water (1 mL; 60 mg·mL⁻¹). The precipitate formed was separated by centrifugation at 4000 rpm for 10 min. The supernatant was decanted and the residue was dried at room temperature.

Octadecylmelamine (OM) was synthesized according to published procedures. Briefly, a mixture of 2-chloro-4,6-diamino-1,3,5-triazine (19 mmol), octadecylamine (19 mmol), and anhydrous sodium hydrogencarbonate (19 mmol) in 1,4-dioxane (75 mL) was refluxed under an argon atmosphere for 6 h. The reaction mixture was then cooled and poured into water (100 mL). The precipitate was filtered off and washed with water. The product was purified by flash chromatography on silica gel, eluting with a dichloromethane/methanol 10:1 mixture.

Synthesis of N-(2-aminoethyl)tricosa-10,12-diynamide (TEA) was carried out according to published methods. Briefly, NHS (3.0 mmol) was added to a solution of TrCDA (2.7 mmol) in CH₂Cl₂ (10 mL), followed by addition of EDC (3.1 mmol). The solution was stirred at room temperature for two hours followed by rotary evaporation of the CH₂Cl₂. The residue was extracted with diethyl ether and water. The organic layer was dried with MgSO₄, filtered, and the solvent was removed by rotary evaporation to give a white solid. The residue (1.28 mmol) in CH₂Cl₂ (20 mL) was added to a solution of 1,2-ethylenediamine (6.60 mmol) in CH₂Cl₂ (25 mL) dropwise, with stirring, over a period of 30 min. The reaction was stirred for an additional 30 min before removal of the solvent by rotary evaporation. The residue was dissolved in ethyl acetate and extracted with water (x 2), and the organic layer was dried with MgSO₄ and the solvent removed by rotary evaporation. The extract was purified by silica gel chromatography (20:1 CHCl₃/MeOH) to give TEA as a white solid. The molecular structures were shown in Figure 1. Water used in the experiments was doubly purified using a Barnstead D7382 water purification system (Barnstead Thermolyne, Dubuque, IA), at 18.3 mCm resistivity.

**Methods**

**In situ monolayer analyses:** Langmuir monolayer measurements were performed using a computerized Langmuir trough (model 622/D1, Nima Technology Ltd., Coventry, UK) at 25 °C. The spreading solvent was chloroform for all the experiments. A solution at a total concentration of 1 mg·mL⁻¹ was spread onto a water surface or aqueous subphase with different pH, as well as aqueous subphases containing different metal ions (1 × 10⁻³ M). After solvent evaporation, the barriers of the trough were compressed at a rate of 10 cm²·min⁻¹.

**Gold microstructures formation on the templates:** Monolayers were transferred onto hydrophobic silica wafer by the Langmuir–Schafer (LS) method. Gold microstructures were assembled by dissolving 28 mg of K[Au(SCN)₄] in water (40 mL) by bath-sonication for 30 min. The monolayer-containing silicon substrates were inserted perpendicularly into the solution in order to reduce non-specific aggregation and incubated for up to 48 h at 4 °C. After removal, the samples were rinsed in water and left to dry at room temperature.

**Brewster angle microscopy (BAM):** A Brewster angle microscope (NFT, Gottingen, Germany) mounted on a Langmuir film balance was used to observe the microscopic structures in situ at the air–water interface. The light source of the BAM was a frequency-doubled Nd:YAG laser with a wavelength of 532 nm and 20–70 mW primary output power in a collimated beam. The BAM images were recorded with a charge coupled device (CCD) camera. The scanner objective was a Nikon superlong working distance objective with a nominal 10× magnification and a diffraction-limited lateral resolution of 2 μm. The images were corrected to eliminate side ratio distortion originating from a non-perpendicular line of vision of the microscope.

**Ex-situ characterization:** Scanning electron microscopy (SEM) images were recorded using a Jeol JSM-7400F Scanning electron microscope (JEOL LTD, Tokyo, Japan) at an acceleration voltage of 3 kV. Atomic force microscopy (AFM) images were recorded at ambient conditions in tapping mode using a Digital Instrument Dimension 3100 mounted on an active anti-vibration table. XPS analysis was carried out using Thermo Fisher ESCALAB 250 instrument with a base pressure of 2×10⁻⁹ mbar. Powder X-ray diffraction (XRD) patterns were obtained using Panalytical Empyrean powder diffractometer equipped with a parabolic mirror on incident beam providing quasi-monochromatic CuKα radiation (λ = 1.54059 Å) and X'Celerator linear detector.

**Conductivity measurements:** 100 μm square electrodes with a spacing of 100 μm, composed of 10 nm Cr and 90 nm Au, were thermally evaporated on glass substrate. Prior to the thermal evaporation the samples were inserted to a plasma cleaner, PDC-32G, Harrick plasma, and were exposed to plasma for 3 min under vacuum. Room-temperature conductivity measurements were carried out in a two-probe configuration using a probe station equipped with a Keithley 4200SCS semiconductor parameter analyzer.

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Diacetylene/surfactant monolayers consisting of $N$-(2-aminoethyl)tricosa-10,12-dynamide (TEA) and octadecylmelamine (OM) produce diverse condensed microstructures upon modulating parameters such as relative amount of the two amphiphiles, subphase pH, and metal ions. Isothermal compression of the monolayers generated rods, flow- ers, disks, fibers, and foam-like structures (see figure).