

Spontaneous formation of discrete arrangement of particles by dipping ultraviolet/ozone-treated poly(dimethylsiloxane) substrate in solution

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ABSTRACT: The spontaneous formation of well-ordered microstructures is an interesting research topic because such formation is useful for cost-effective production of functional materials. In this article, we report a novel method for spontaneous formation of a discrete arrangement of particles using an ultraviolet/ozone-treated poly(dimethylsiloxane) substrate. The substrate was first dipped in a solution (solvent: mixture of methanol and water, solute: sucrose or lithium perchlorate) in a sealed vessel filled with the vapor of the solvent, and was then dried in air to precipitate the solute as particles. In spite of the simplicity of the procedure, the particles were regularly and discretely arranged in a triangular lattice with a distance between the neighboring particles of about 48 μm . The mechanism of formation of the array was explained by considering the formation of regular dimples due to swelling of the substrate surface with the solution and the dewetting of the liquid film of the solution on the surface. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43506.

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INTRODUCTION

Well-ordered arrays of micrometer- or nanometer-size objects (mainly particles,¹ but sometimes discs,² pillars,³ holes,⁴ etc.), have attracted extensive attention in various fields including materials science,^{1,5} electronics,⁶ and analytical chemistry.² The sizes of the objects employed for such arrays range from several nanometers (e.g., quantum dots)⁷ to submicrons (e.g., colloidal spheres of polymers)¹ and even one millimeter (e.g., silicon spheres for solar cells).⁸ One,^{9,10} two,¹¹ or three¹ dimensional arrays have been constructed with a wide variety of materials, including metals,¹² semiconductors,⁸ inorganic compounds,¹³ organic compounds,⁶ polymers,¹⁴ biological molecules,¹⁵ and even cells.¹⁶

Three-dimensional and closely packed arrays of colloidal spheres comprising photonic crystals are well-known and widely studied examples of well-ordered arrays of small objects.¹⁷ However, in this study, we are interested in two-dimensional, discrete arrangements of particles. According to the literature, examples of small objects arranged in such a manner include iron oxide nanoparticles used as catalysts for carbon nanotube growth,¹⁸ cobalt nanopillars for patterned media,³ aluminum particles for nano-antennas,¹⁹ silicon spheres for solar cells,⁸ microdisks for electrochemical analyses,² and cells for single-cell analyses.¹⁶

Methods for forming such a regular, discrete pattern often utilize lithographic techniques, such as photolithography¹⁶ and electron beam lithography.¹⁸ However, spontaneous formation of regular patterns is also employed and is advantageous for low-cost manufacturing. For example, regular nanohole arrays formed by the anodic oxidation of aluminum,²⁰ and ordered domains of block copolymers formed by microphase separation have been used.²¹ The obtained regular patterns are utilized as templates for arranging small objects during the next step. In addition, dendrimer nanodot arrays were formed by solvent evaporation²² and polyethylene nanodot arrays were prepared using the friction rubbing method.²³

In this study, we develop a novel method wherein both (1) spontaneous formation of regular templates and (2) arrangement of small droplets occur during a single process; particles as well as droplets can be arranged by drying the droplets, provided the droplets contain some solute. (1) The spontaneous formation of regular templates was achieved by exploiting the swelling of a poly(dimethylsiloxane) (PDMS) surface that was pretreated with ultraviolet/ozone (UVO). As reported,^{24–26} such PDMS surfaces can be swollen with polar solvents and consequently be deformed to generate wrinkles or dimples. Although we use dimples for arranging the droplets in this study, Fery et al. reported the assembly of colloidal particles using

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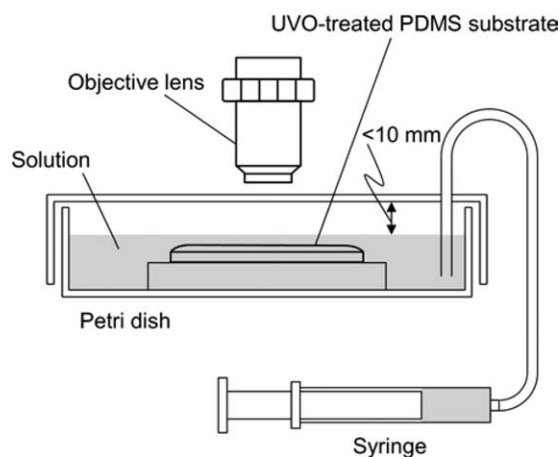


Figure 1. Method for observing substrate immersed in solvent using light microscope.

wrinkles.¹⁰ (2) The arrangement of small droplets was realized using dewetting. Dewetting of liquid films^{6,27,28} and solid films (i.e., solid-state dewetting)^{29–31} has become topical in recent years because of the variety of potential applications, including the production of micro- or nanoparticles and the regular arrangement of such particles.^{32–34} In this study, we combine the swelling of the UVO-treated PDMS surfaces and the dewetting of liquid films. Thus, we could successfully obtain regularly arranged particles using a facile, single process.

EXPERIMENTAL

Preparation of the UVO-treated PDMS Substrate

The precursor of PDMS (KE-103) and the curing agent (CAT-103) were purchased from Shin-Etsu Chemical (Tokyo, Japan). The precursor and the curing agent were mixed in a mass ratio of 100:2 and degassed under vacuum. A portion of this mixture (0.7 g) was cast on a rectangular glass slide (43 mm × 26 mm, 1-mm thick). The glass slide was stored at room temperature for 2 h and then vulcanized in an oven at 100 °C for 2 h. The obtained PDMS substrate, which was employed for all the following experiments without being peeled off from the glass slide, was subjected to the UVO treatment for 50 min using a UV/ozone cleaner (UV-TC-110, Bioforce Nanosciences, Ames, IO). The distance between the UV lamp of the cleaner and the PDMS substrate was around 2.4 cm. The UVO-treated PDMS substrate was immediately employed for the following experiments to avoid errors from changes in the surface property with the passage of time.³⁵

Observation of the Substrate Surface Immersed in Solvent

The UVO-treated PDMS substrate was placed in a Petri dish (Figure 1). The lid of the dish had a small hole, through which a syringe was used to inject solvent into the dish while a light microscope (MELUX-2-1L, Kyowa Optical, Kanagawa, Japan) was used to observe the surface of the substrate immersed in the solvent without opening the lid. The solvent was typically composed of methanol and water [e.g., methanol: water = 100:24 (mass ratio)]. After several minutes, the syringe was used to remove the solvent until the solvent no longer covered the substrate surface; this was also carried out without opening the lid and the observation was continued.

Dipping of the Substrate in Solution

A solution composed of methanol, water, and sucrose (in a mass ratio of 100:26:5) was prepared in a sealed vessel (Figure 2). The vessel was stored at room temperature for at least 1 hr to fill the space above the solution with the vapor of the solvent. This was because the height of the vacant space in the sealed vessel was about 70 mm (Figure 2), which was much higher than that in the Petri dish (<10 mm, see Figure 1). The UVO-treated PDMS substrate was fixed on the tip of an aluminum bar using double-sided adhesive tape and inserted into the sealed vessel. The substrate was first suspended above the surface of the solution and then dipped into the solution at a speed of 20 mm min⁻¹ using an electronically controlled dipper (KN0055, KSV Instruments, Helsinki, Finland). After 10 s, the substrate was withdrawn at the same speed. The substrate was then dried in air at room temperature for 1 h. Similar experiments were performed using a solution composed of methanol, water, and lithium perchlorate.

Examination of the Surface Using a Scanning Probe Microscope

The substrate that was dried after dipping in the sucrose solution was observed using a scanning probe microscope (SPA-400, Hitachi High-Tech Science Corporation, Tokyo, Japan) in dynamic force mode. Because of the easy build-up of static electricity on the substrate, which disturbed the measurements, the substrate was coated with a gold thin film using a DC sputtering coater (IB-3, Eiko Engineering, Hitachinaka, Japan) at a coating rate of 1.8 nm min⁻¹ for 0.5 min prior to the measurement.

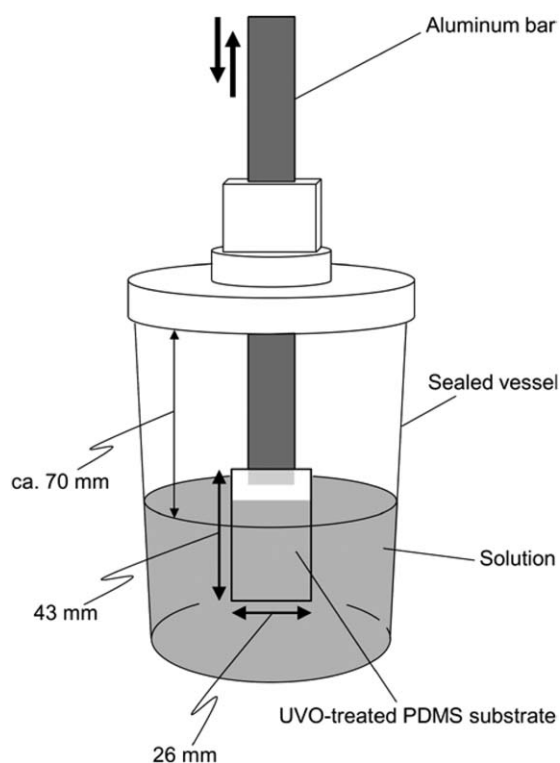


Figure 2. Schematic diagram of sealed vessel used for dipping substrate in solution.

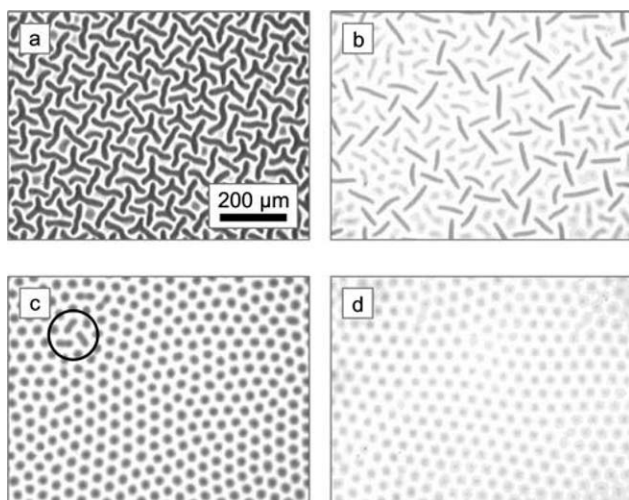


Figure 3. Light microscope images of UVO-treated PDMS substrates immersed in (a) methanol and (b)–(d) methanol and water mixtures. The mass ratios of methanol to water were (b) 100:20, (c) 100:24, and (d) 100:28.

Measurement of Infrared (IR) Absorption Spectra

IR spectra were collected using a Fourier transform infrared spectrometer (FTIR-8400, Shimadzu Corporation, Kyoto, Japan) in attenuated total reflection (ATR) mode with a KRS-5 crystal with an angle of incidence of 45°.

X-ray Photoelectron Spectra

X-ray photoelectron spectra were acquired using an X-ray photoelectron spectrometer (Axis-ultra DLD, Kratos Analytical, Manchester, UK) with Mg K α radiation. Charge neutralization was carried out during the measurement. Linear background subtraction was carried out before calculating the atomic composition.

RESULTS AND DISCUSSION

Examination of Solvent Composition for forming Dimples

When the UVO-treated PDMS substrate was immersed in methanol, unidirectional short grooves (typically 100- μ m long and 17- μ m wide) were formed on the surface [Figure 3(a)]. Cai et al. reported similar results after exposing UVO-treated PDMS substrates to ethanol vapor, and attributed the results to the swelling of the surface layer oxidized by the UVO treatment with ethanol.²⁵ On the other hand, when the substrate was immersed in water, the surface remained flat. Thus, methanol was a good solvent and water was a poor solvent for the oxidized surface layer. Therefore, swelling the surface layer was examined using mixtures of methanol and water with various ratios. At a methanol to water mass ratio of 100:20, both the short grooves and the dimples (ca., 23 μ m in diameter) were observed [Figure 3(b)]. For ratios of 100:24 or 100:28, only dimples with a constant diameter were arranged over the entire surface [Figure 3(c,d)]. When the water content was further increased (100:32), no dimples were formed and the surface remained flat. Thus, the ratio of methanol to water could be judiciously varied to control the surface topography.

Light Microscopy Observation of the Surface after the Removal of Solvent

As shown in Figure 1, the UVO-treated PDMS substrate was placed in a Petri dish covered with an optically transparent lid. A methanol and water mixture was then injected into the dish through a small hole of the lid until the substrate totally sank under the solvent. After 5 min, the solvent was removed through the hole without opening the lid. During the series of these operations, the substrate surface was observed through the lid using a light microscope. Droplets were thus left in the dimples and short grooves (Figure 4). Figure 4(a) shows the receding contact line of the solvent, which divided the image into two areas. In the upper right area, the surface was covered with the solvent. In the lower left area, droplets were left in the dimples and short grooves as the solvent receded. Although Figure 3(c) shows dimples under the solvent, Figure 4(b) shows droplets formed in the same area. The distance between neighboring dimples was the same as that between neighboring droplets. The characteristic arrangement of the dimples indicated by the circle in Figure 3(c) was also retained in Figure 4(b). These results indicate that the dimples and short grooves act as templates for arranging the droplets.

Given the rapid disappearance of the droplets due to solvent evaporation after opening the lid, solid solutes were introduced by dissolution in the solvent. Sucrose and lithium perchlorate (LiClO₄) were employed as examples of organic and inorganic solutes. The optimum ratio of methanol to water for forming the dimples varied slightly based on the solute employed and its concentration. Figure 5 shows (a) dimples formed when the substrate was immersed in a sucrose solution (mass ratio of methanol:water:sucrose = 100:26:5), (b) droplets formed when the solution was removed without opening the lid of the Petri dish, (c) solid sucrose particles precipitated due to evaporation of the solvent after opening the lid, and (d) a magnified view of these particles, which are called “microprecipitates” hereafter. The average diameter of the sucrose microprecipitates was 5.6 μ m and the average distance between the neighboring microprecipitates was 55 μ m. When lithium perchlorate was used as the solute, similar microprecipitates were obtained (Figure 6). The average diameter and distance were 7.2 and 48 μ m, respectively. Other solutes may be employed for the same purpose, provided they are soluble in the methanol and water mixture. In this

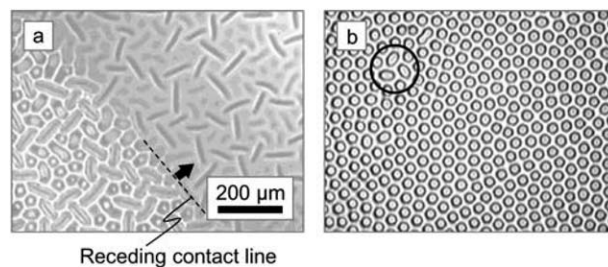


Figure 4. Light microscope images of UVO-treated PDMS substrates. The substrates were first immersed in the solvent (a mixture of methanol and water) and observed during and after removal of the solvent. Mass ratios of methanol to water were (a) 100:20 and (b) 100:24.

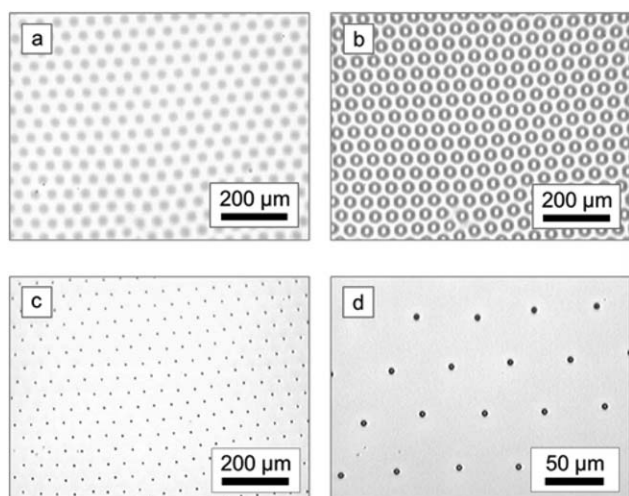


Figure 5. Light microscope images of (a) dimples induced by swelling of the UVO-treated PDMS substrate with sucrose solution (b) droplets formed when the solution was removed, and (c,d) sucrose microprecipitates formed after evaporation of the solvent. The composition of the solution was methanol:water:sucrose = 100:26:5 (mass ratio).

experiment, the sealed condition (that is, closing the lid of the Petri dish) was required for formation of the microprecipitates, as discussed in a later section.

Sucrose microprecipitates were formed by drying droplets of solutions with various concentrations and observed using a light microscope to measure their diameters. A smaller diameter was observed with decrease in solute concentrations [Figure S1(a–c) in the Supporting Information]. Assuming that the volume of the droplet is not affected by the concentration and the microprecipitates have similar shape, the diameter of the microprecipitate is predicted to be proportional to the cube root of the concentration. As shown in Figure S1(d) (in the Supporting Information), the relationship between the measured diameter and the concentration was consistent with this prediction. Thus, the diameter could be controlled by varying the solute concentration.

Development of a Dip Method for a More Ordered Arrangement of Microprecipitates

As shown in Figures 3(c), the dimples were aligned along the distorted lines [see also Figure S2(a) in the Supporting Information]. This figure was obtained by adding the curved lines to Figure 3(c)]. Therefore, we tried to find a method to remove this distortion.

Dimples were quickly formed upon contact of the surface of the UVO-treated PDMS substrate with the solution. Therefore, the shape of the contact line of the solution on the substrate seemed to affect the arrangement of the dimples. We postulated that a straight contact line would be preferable for achieving precise arrangement of the microprecipitates than a curved line. To obtain a straight contact line, the substrate was vertically suspended and slowly dipped into the solution using an electronically controlled dipper at a constant dipping speed of 20 mm min^{-1} . This dipping process was carried out in a sealed vessel filled with the vapor of the solvent (Figure 2). After withdrawal of the sample from the

solution at the same speed, the substrate was removed from the vessel and dried in air. Well-ordered microprecipitates of sucrose were thus obtained over a wide area (at least 3 cm^2), as shown in Figure 7 (high magnification images) and Figure S3 in the Supporting Information (low magnification images). As can be seen by comparing Figure S2(a,b) shown in the Supporting Information, the regularity of the arrangement was significantly improved. [Supporting Information Figure S2(b) was obtained by adding straight lines to Supporting Information Figure S3(f)]. The microprecipitates adopted a triangular lattice arrangement with an average distance between the neighboring microprecipitates of $48.4 \mu\text{m}$, and on overall distance range of 46.3 to $52.2 \mu\text{m}$. The average diameter of the microprecipitates was $6.5 \mu\text{m}$, with an overall range of 5.4 to $7.4 \mu\text{m}$.

Regularly organized microprecipitates were also obtained when lithium perchlorate was used as a solute (Figure S4 in the Supporting Information). However, sometimes needle-like crystals formed on the surface if the sample was exposed to ambient atmosphere for more than 40 min [Supporting Information Figure S4(p)]. In addition, the surface was examined after 18 days using XPS (Figure S5 in the Supporting Information). The spectrum showed two peaks for Cl 2p at 197 eV and 206 eV, which were assigned to Cl^- and ClO_4^- , respectively.³⁶ Therefore, lithium perchlorate was partially decomposed on the surface.

Surface Analyses of UVO-treated PDMS Substrate Using Infrared Absorption Spectroscopy and X-ray Photoelectron Spectroscopy

IR spectra of the untreated and UVO-treated PDMS were collected using the attenuated total reflection (ATR) method. Detailed studies on the IR spectra of UVO-treated PDMS have been reported.^{37,38} We have obtained similar results, as shown in Figure 8. The absorption band at 1081 cm^{-1} , which was assigned to the asymmetric stretching of the siloxane bond (Si-O-Si), increased in intensity after the UVO treatment. This result suggests that a silica-like material was formed by the oxidative cleavage of the methyl groups in the PDMS chain. The band assigned to hydroxyl groups ($3050\text{--}3700 \text{ cm}^{-1}$) was observed for the UVO-treated PDMS. These results suggest that the UVO treatment made the surface hydrophilic, which caused the surface to swell in the presence of a polar solvent such as methanol.

X-ray photoelectron spectroscopy (XPS) was employed to compare the atomic composition of the UVO-treated PDMS with that of the untreated sample. As summarized in Table I, the

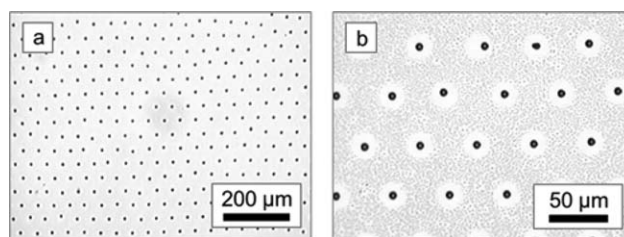


Figure 6. Light microscope images of lithium perchlorate microprecipitates under (a) low and (b) high magnification. The composition of the solution employed in this experiment was methanol:water:lithium perchlorate = 100:22:5 (mass ratio).

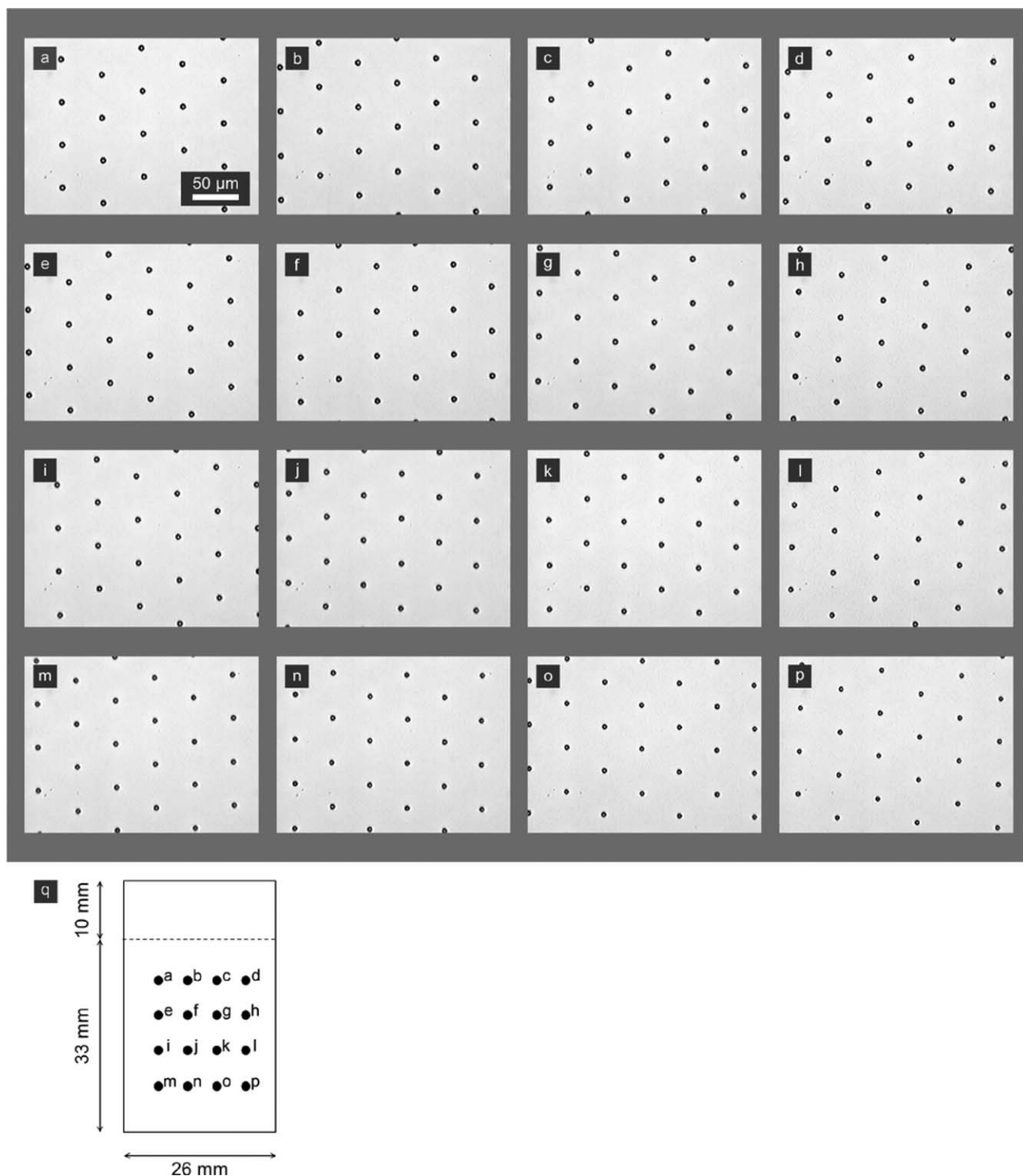


Figure 7. (a–p) Light microscope images of well-ordered sucrose microprecipitates formed using dip method. (q) Observed positions on the substrate for images a to p. The methanol:water:sucrose mass ratio of the solution was 100:26:5. The part of the substrate under the broken line indicated in q was dipped into the solution.

UVO treatment decreased the carbon content and increased the oxygen content, suggesting that the methyl groups in PDMS were oxidatively cleaved. This result is consistent with the changes observed in the IR spectra. Olah et al. have also reported similar results using XPS.³⁹

Possible Mechanism for Arranging Microprecipitates

The three dimensional morphology of the solid sucrose microprecipitates was evaluated using scanning probe microscopy (Figure 9). The shape of the microprecipitate particle could be approximated by a spherical segment. The height (h) and base

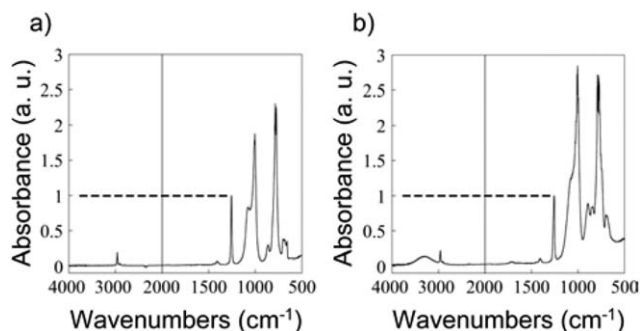


Figure 8. Infrared spectra of (a) untreated and (b) UVO-treated (for 120 min) PDMS substrates collected using the ATR method. The spectra were normalized to fix the absorbance of the peak at 1257 cm^{-1} (symmetric deformation of CH_3) to 1.

diameter ($2r$) were typically 0.83 and $6.3\text{ }\mu\text{m}$, respectively [Figure 10(a)]. The volume (V_{mpr}) of this precipitate particle was estimated to be $1.3 \times 10^{-11}\text{ cm}^3$ using the following equation:

$$V_{\text{mpr}} = \pi h(h^2 + 3r^2)/6 \quad (1)$$

Based on this value, the volume of solution (V_{sol}) required to form each microprecipitate particle by evaporation of the solvent was calculated to be $6.5 \times 10^{-10}\text{ cm}^3$ using the following equation:

$$V_{\text{mpr}} d_{\text{mpr}} = V_{\text{sol}} d_{\text{sol}} f \quad (2)$$

where d_{mpr} and d_{sol} are the respective densities of the microprecipitate (1.59 g cm^{-3} for sucrose) and the solution (0.85 g cm^{-3} for the solution with sucrose:water:methanol mass ratio of 5:26:100), and f is the mass fraction of solute in the solution (0.038 for the sucrose solution).

Here, formation of the microprecipitate is tentatively assumed to progress according to the steps shown in Figure 10(b). Initially, a liquid film of the solution continuously covers the entire surface of the UVO-treated PDMS substrate. The film is divided into imaginary hexagonal cells where the distance between opposite sides, d , [Figure 10(b)] is equal to the distance between the neighboring microprecipitates [Figure 10(a)]. A droplet forms from each cell and then shrinks to become a solid microprecipitate particle due to evaporation of the solvent [Figure 10(b)]. For each hexagonal cell, the thickness of the liquid film, t , is expressed as:

$$t = V_{\text{sol}}/S \quad (3)$$

where S is the area of the hexagon expressed by:

$$S = \sqrt{3}d^2/2 \quad (4)$$

Therefore, t is estimated to be $0.32\text{ }\mu\text{m}$.

Table I. Atomic Composition of Untreated and UVO-treated PDMS Substrate Surfaces Calculated from X-ray Photoelectron Spectra

UVO treatment time (min)	Atomic composition (atom %)		
	C	O	Si
0	52.0	23.7	24.3
60	43.2	31.9	24.9
90	33.1	41.1	25.9

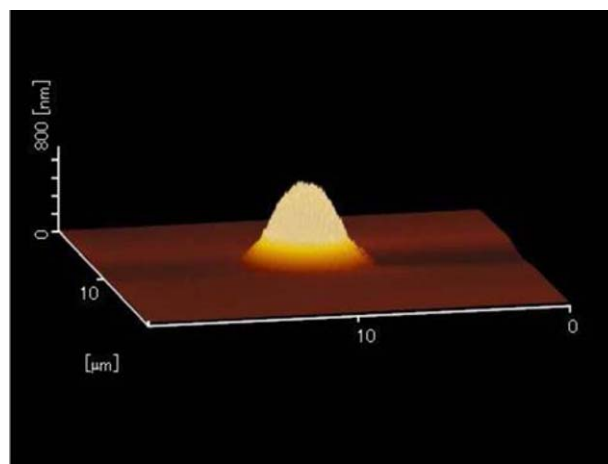


Figure 9. Scanning probe microscope image of sucrose microprecipitate particle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Although the depth of the dimple was not measured in this study, Breid and Crosby presented 3D images of dimples with similar diameters (ca., $50\text{ }\mu\text{m}$) that were also formed on a UVO-treated PDMS substrate by swelling.²⁴ The depth determined from these images was around $0.6\text{ }\mu\text{m}$. This was roughly comparable to the thickness of the liquid film ($0.32\text{ }\mu\text{m}$) estimated above.

Therefore, we propose a plausible mechanism for microprecipitate formation as follows: when the UVO-treated PDMS substrate is immersed in the solution, the surface becomes swollen with the solution and dimples are formed [Figure 11(a)]. By removing excess solution from the Petri dish or by withdrawing the substrate from the solution, a liquid film is formed [Figure 11(b)]. Because the mean thickness of the liquid film is comparable to the

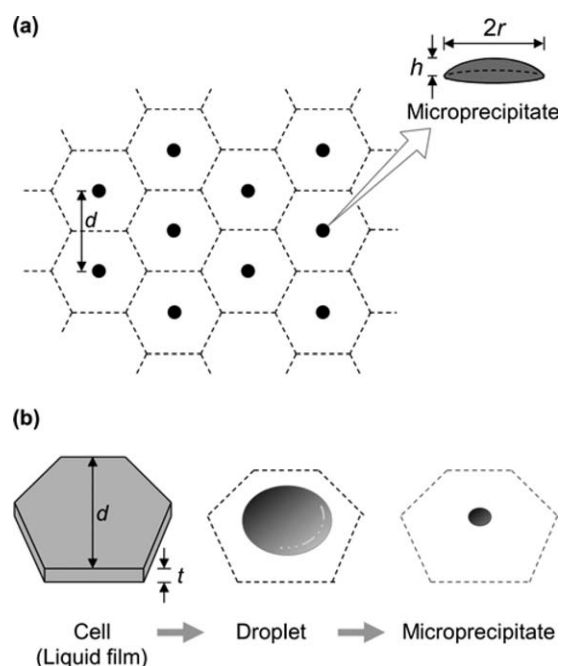


Figure 10. Schematic diagrams of (a) dimension of microprecipitates and (b) formation of microprecipitate from liquid film.

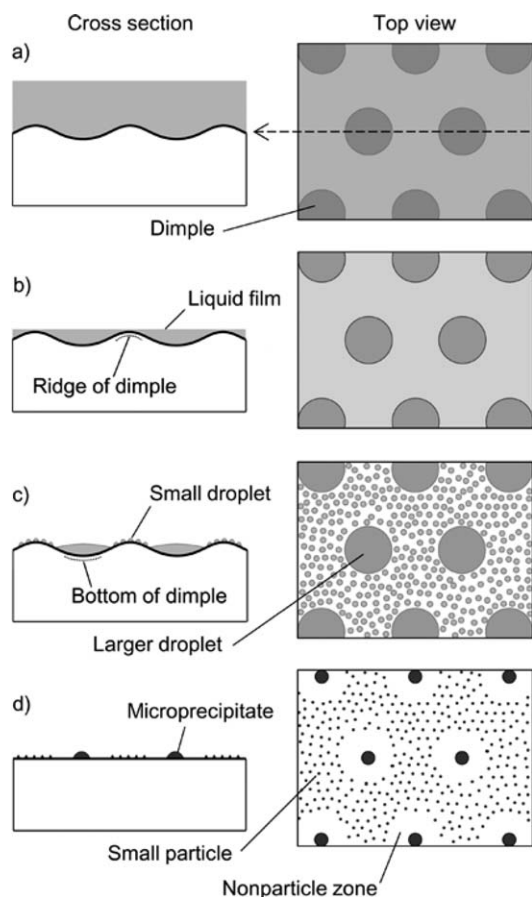


Figure 11. Possible mechanism for formation of microprecipitates. (a) Swelling of surface, (b) formation of liquid film, (c) dewetting, and formation of larger droplets, and (d) formation of microprecipitates by evaporation of solvent.

depth of the dimple as stated above, the film on the elevated part of the substrate (i.e., on the ridge of the dimple) is considerably thinner than that on the bottom of the dimple. As reported by Kargupta and Sharma,²⁷ on such a topographically inhomogeneous surface, the liquid film on the elevated part of the surface is less stable than that on other part. Therefore, the part of the film on the ridge of the dimple is converted into small droplets due to dewetting [Figure 11(c)]. As a result, the other part is divided into larger droplets, which are trapped in the troughs of the dimples. During the succeeding evaporation of solvent by opening the lid of the Petri dish or taking the substrate out of the sealed vessel, each larger droplet shrinks to form a microprecipitate of the solute [Figure 11(d)]. The small droplets are then also dried, leaving small particles.

Based on the mechanism presented above, it is predicted that after evaporation of the solvent, small particles will be left on the region that was originally the ridge of the dimple. In addition, because the larger droplets shrink due to evaporation, there will be a nonparticle zone around the microprecipitate [Figure 11(d)]. These two predicted features (i.e., small particles and a nonparticle zone) were observed when both LiClO_4 and sucrose were used as solutes [Figure 6(b) and Figure S6 in the

Supporting Information], although the distinct regions were not very clear in the case of sucrose. These results support the mechanism proposed above.

As described in a previous section, the method developed in this study requires an atmosphere of the solvent vapor. That is, the lid of the Petri dish should be closed and the dipping process should be performed in a sealed vessel. As shown in Figure 4, arrangement of the droplets occurred in the vapor of the solvent before drying in air. Although methods for spontaneous formation of regular structures from solution have been reported by many groups, these prior approaches were mainly based on phenomena occurring during evaporation of the solvent in air, such as the stick-slip motion and the fingering instability.^{40,41} Thus, the present method, carried out in the vapor of the solvent, is significantly different from other methods performed in air.

Here, we attempt to explain why the sealed condition is necessary in the present method. Under the open condition, the gas phase is air and the liquid phase is the solvent, while under the closed condition, the gas phase is the vapor of the solvent itself. Therefore, the interfacial free energy between the gas and liquid phases under the closed condition is smaller than that under the open condition. This means that the liquid film formed after removal of the excess solution [Figure 11(b)] is more stable under the closed condition than under the open condition (to simplify the discussion, evaporation is not considered here). Because more stable products are generally more easily produced, formation of the liquid film is also easier under the closed condition. Based on the mechanism proposed above (Figure 11), without formation of the liquid film, the microprecipitates will not form. Therefore, the sealed condition is requisite for formation of the microprecipitates.

CONCLUSIONS

Solvent mixtures comprising methanol and water effectively induced swelling of the surface of the PDMS substrate pretreated with UVO. With the use of an appropriate solvent composition, dimples with a regular diameter were effectively formed on the PDMS surface. Removal of the solvent from the PDMS surface under the solvent vapor left a droplet of the solvent in each dimple. Microprecipitates of the solute with a diameter of several micrometers were generated after drying the surface when solutes such as sucrose and lithium perchlorate were dissolved in the solvent. Regularly arranged microprecipitates with a constant spacing were also formed by dipping the PDMS substrate into the solvent in a sealed vessel filled with the vapor of the solvent. This dipping method is very simple and cost-effective and is prospectively applicable in the fabrication of disposable chemical or biochemical array sensors.⁴² The high regularity of the arrangement of the microprecipitates obtained by this method offers advantages, such as good addressability of each microprecipitate, which may be useful for single cell analyses if cells can be arranged by this method.¹⁶

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