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Fabrication of Large-Area Hierarchical Structure Array Using Siliconized-Silsesquioxane as a Nanoscale Etching Barrier

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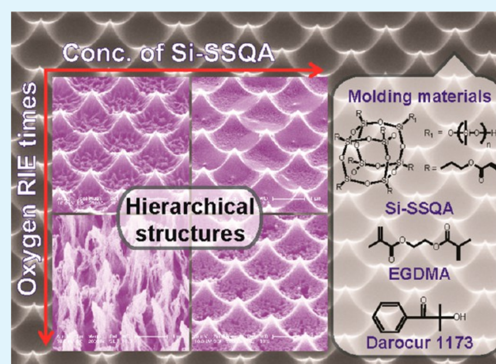
Supporting Information

ABSTRACT: A material approach to fabricate a large-area hierarchical structure array is presented. The replica molding and oxygen (O_2) plasma etching processes were combined to fabricate a large-area hierarchical structure array. Liquid blends consisting of siliconized silsesquioxane acrylate (Si-SSQA), ethylene glycol dimethacrylate (EGDMA), and photoinitiator are developed as a roughness amplifying material during O_2 plasma etching. Microstructures composed of the Si-SSQA/EGDMA mixtures are fabricated by replica molding. Nanoscale roughness on molded microstructures is realized by O_2 etching. The nanoscale roughness on microstructures is efficiently controlled by varying the etching time and the weight ratio of Si-SSQA to EGDMA. The hierarchical structures fabricated by combining replica molding and O_2 plasma etching showed superhydrophilicity with long-term stability, resulting in the formation of hydroxyl-terminated silicon oxide layer with the reorientation limit. On the other hand, the hierarchical structures modified with a perfluorinated monolayer showed superhydrophobicity. The increment of water contact angles is consistent with increment of the nano/microroughness of hierarchical structures and decrement of the top contact area of water/hierarchical structures.



KEYWORDS: *hierarchical structures, replica molding, silsesquioxane, oxygen plasma etching, superhydrophilicity, superhydrophobicity, large-area production*

■ INTRODUCTION

The modulation of surface wettability has recently attracted a great deal of attention for fundamental understanding practical applications.[1−5] Superhydrophobicity and superhydrophilicity are often considered to modulate surface wettability. The surface wettability is expressed by the contact angle of a water droplet on the surface. Surfaces with water contact angles (WCAs) less than 5° are defined as superhydrophilic surfaces. These properties are of special interest for various outdoor and indoor applications, such as antifogging, antifouling, and photocatalytic self-cleaning.[1,2] In contrast, surfaces with WCAs higher than 150° are usually called the superhydrophobic surfaces. Superhydrophobic surfaces with water repellency and self-cleaning functions plays critical roles in a wide range of applications, such as self-cleaning windows for the automotive and aeronautics industries,[6,7] waterproof textiles,[8] antibiofouling paints for marine organisms,[9] antisticking of snow for antennas and windows,[10] antifingerprint film,[11] antireflective coating,[12] anti-icing coating,[13] anticorrosion coating,[14] oil/water separation, and so on.[15]

It was generally known that surface roughening plays an important role for the surface wettability. Hierarchical structures with a multiscale roughness were commonly observed on superhydrophilic and superhydrophobic surfaces.[1] Therefore, much research has been performed to create hierarchical structures with multiscale roughness based on top-down, bottom-up and combination methods.[3−6] The bottom-up methods encompass self-assembly,[16] layer-by-layer assembly,[17] micelle aggregation,[18] phase separation,[19,20] electrochemical deposition,[21] and atmospheric pressure plasma deposition.[22−24] One of the major advantages of such bottom-up methods based on self-assembly or self-organization is that they provide an easy and efficient route to generating multiscale hierarchical structures on a large-area. In addition, nanostructures with feature sizes of a few tens of nanometers can be formed in a hierarchical structure without the use of expensive and complicated processes. However, these methods are often limited by the limited design capability of hierarchical structures and the lack of precise control of geometrical parameters such as a size, shape, pitch, and heights of nano/microstructures, because these methods generate randomly oriented hierarchical structures. In contrast, top-down methods including photolithography,[25,26] mold-based lithography,[27−29] and plasma etching of the surfaces[25,30−32] offer an efficient route to the fabrication of well-defined nano- or microscale structures by using predetermined patterns of a mask or mold.

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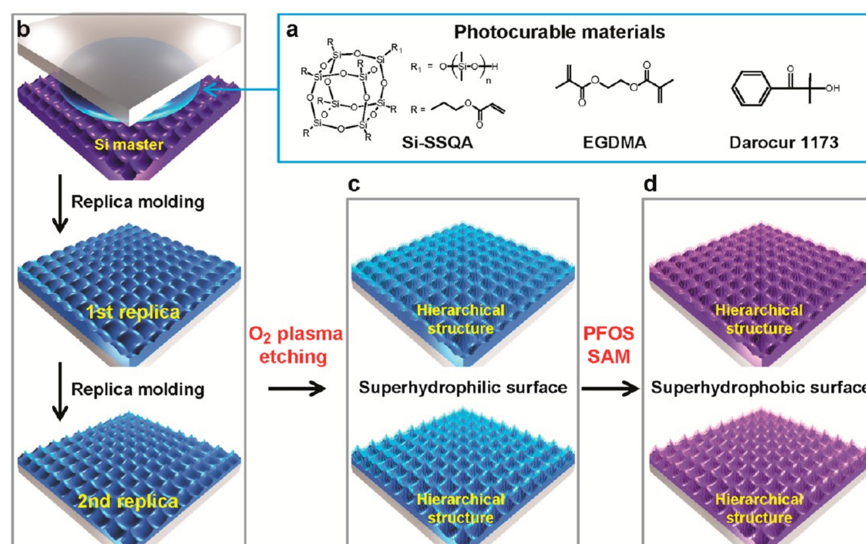

Figure 1. Schematic illustration of the procedure for the fabrication of the hierarchical structures with superhydrophilicity or superhydrophobicity. (a) Chemical structures of the photocurable precursors. Siliconized cubic silsesquioxane acrylate is indicated as a typical Si-SSQA. (b) Schematic illustration of the UV-assisted replica molding process for the fabrication of microstructures. (c) Microstructures are etched by oxygen plasma to prepare hierarchical structures with superhydrophilicity. (d) Hierarchical structures are modified with PFOS SAM to create superhydrophobic surfaces.

However, despite the advantages of top-down methods, there are some restrictions that have prevented their widespread use. For example, the photolithographic methods are often expensive and only applicable to small flat surfaces or specific materials.[20] Mold-based lithographic techniques, such as nanoimprint lithography and replica molding are a cost-effective and reliable way of fabricating microstructure over large areas[28,29] and can provide precision on the order of 8 nm.[33] However, when the pattern size is reduced to a nanoscale from a microscale, careful manipulation is required to avoid damaging samples and expensive high-quality molds. In addition, plasma treatment under a vacuum requires a great deal of trial and error to produce surfaces with complex roughness. The methods based on the combination of top-down and bottom-up methods, such as two-step photolithography,[34] two-step micro/nanosphere lithography,[35] multilevel anionic etching of aluminum oxide,[36] the combination of microsphere lithography and electrochemical deposition,[37] and two-step mold-based lithography,[28,29] were developed to fabricate hierarchical structure arrays. This is because hierarchical structure arrays have great potential applications in many fields, such as catalysis, integrated nanophotonics, optical devices, superhigh-density storage media, sensors, nanobiotechnology, surface-enhanced Raman scattering substrates, and so forth.[38] However, two-step photolithography, two-step micro/nanosphere lithography, and multilevel anionic etching of aluminum oxide required a time-consuming two-step etching to fabricate hierarchical structure arrays. In addition, two-step micro/nanosphere lithography, multilevel anionic etching of aluminum oxide, and the combination of microsphere lithography and electrochemical deposition have a limited design capability for the production of hierarchical structure arrays. Furthermore, it is difficult to make nanoscale roughness in a recessed area by two-step mold-based lithography. Upon this background, an inexpensive and efficient way to fabricate well-defined hierarchical structures for large-area use would be particularly useful for a wide range of applications.

The goal of this study was to develop a simple, cost-effective way to fabricate regularly arrayed hierarchical structures with superhydrophilic or superhydrophobic properties for large-area application. Here, a combination of mold-based lithography and reactive ion etching was used to fabricate regularly arrayed hierarchical structures with multiscale roughness. This combination has many advantages to fabricate hierarchical structure arrays, such as simplicity, abundant design capability, short processing time (<15 min), needlessness of resist lift-off process, high throughput, high yield, high uniformity, and low-cost large area processability. The ultraviolet (UV)-assisted replica molding method was used to fabricate regularly arrayed microstructures (Figure 1b). The O_2 plasma etching with a potential for large-area application was used to fabricate the nanoscale roughness on the prepatterned microstructures (Figure 1c). The liquid blends consisting of siliconized silsesquioxane acrylate (Si-SSQA), ethylene glycol dimethacrylate (EGDMA), and photoinitiator were developed as a replica molding material to amplify the nanoscale roughness during O_2 plasma etching process. The surface roughness change of the cured Si-SSQA/EGDMA mixtures was discussed in terms of the weight ratio of Si-SSQA and etching time. The hierarchical structures with multiscale roughness were utilized as superhydrophilic and superhydrophobic surfaces. As demonstrated in the following, the combined approach of mold-based lithography and O_2 plasma etching provides an effective and inexpensive way to fabricate regularly arrayed hierarchical structures over a large area.

■ EXPERIMENTAL SECTION

Materials. Si-SSQA (AC-SQ SI-20) was purchased from Toagosei Co., Ltd., Darocur 1173 (2-hydro-2-methyl-1-phenyl-1-propane) as a photoinitiator was provided by Ciba Specialty Chemicals. EGDMA and trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl) silane (PFOS) were purchased from Sigma-Aldrich.

Preparation of a Photocurable Mixture. The UV curable prepolymer used for the UV-assisted replica molding in this work is a liquid mixture of Si-SSQA and EGDMA. Additionally, Darocur 1173

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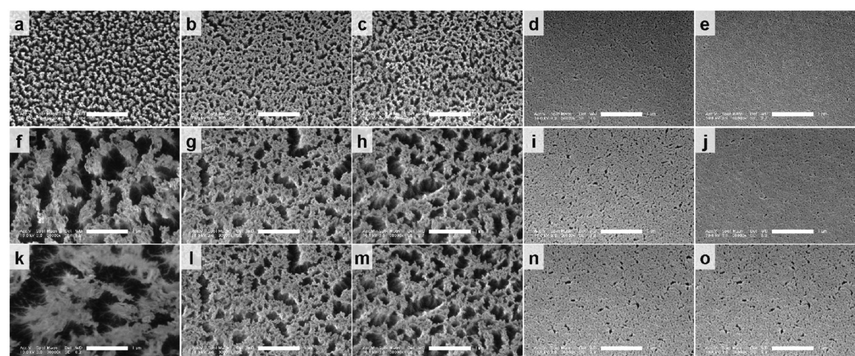

Figure 2. SEM images of cured Si-SSQA/EGDMA mixtures after O_2 plasma etching for (a−e) 1 min, (f−j) 5 min, and (k−o) 10 min when the ratio of Si-SSQA is (a, f, k) 2.5 wt %, (b, g, l) 5 wt %, (c, h, m) 10 wt % (d, i, n), 20 wt %, and (e, j, o) 30 wt %. The scale bar is 1 μm.

was simply blended at 5 wt % with respect to the total amount of the blend of Si-SSQA and EGDMA.

Replica Molding Processes. A suitable amount of the Si-SSQA/EGDMA mixtures containing 5 wt % photoinitiator was drop-dispensed onto a Si-master mold modified with PFOS self-assembled monolayer (SAM). The transparent substrates such as polyethylene terephthalate (PET) film and glass were carefully placed on top of the liquid mixtures. The samples were subsequently cured by UV irradiation at a wavelength of 365 nm for 5 min with a 250 W ultrahigh-pressure mercury lamp. After UV curing, the Si-SSQA/EGDMA blends replicated on transparent substrates were peeled from the master mold. The first replicas composed of the Si-SSQA/EGDMA mixtures on transparent substrates were used as a stamp to fabricate the second replicas composed of the Si-SSQA/EGDMA mixtures using the UV-assisted replica molding method.

O_2 Plasma Etching. To create nanoscale roughness on photocured micropatterns, O_2 plasma etching process was used. The O_2 plasma etching was carried out at 50 mTorr total gas pressure, an O_2 gas flow rate of 10 standard cubic centimeters (sccm), and radio frequency power of 100 W using a reactive ion etching system (URS Series, Ultech Co., Ltd.).

SAM Treatment. To create a superhydrophobic surface, the surfaces of the first and second replicas treated with O_2 plasma were modified with a hydrophobic material. PFOS as a hydrophobic material was modified to the surface of the replicas in a vacuum chamber at 110 °C for 1 h.

Observation of Pattern Morphology. Field emission scanning electron microscopy (FE-SEM, Sirion 400, FEI) was used to observe the surface morphology of the nano- and micropatterns. To prevent charging, the samples were coated with a 10 nm gold layer prior to analysis. The surface roughness was analyzed by atomic force microscope (AFM, Veeco Dimension 3100, Digital Instrument Ltd.) in tapping mode in air. The data, such as the root-mean-square (RMS) roughness and height image, were processed using n-Surf software.

WCA Measurement. The surface wetting properties were evaluated using a contact angle analyzer (Phoenix-300, Surface Electro Optics Co., Ltd.) with image XP software. The WCAs were measured in the ambient atmosphere by the sessile drop and captive droplet methods. It was observed that the WCAs measured by the captive droplet method were about 1−3° higher for the same sample than the WCAs measured by the sessile drop method. At least five measurements were performed for each sample, and the results were averaged.

■ RESULTS AND DISCUSSION

Figure 1 illustrates the process for fabricating the monolithic hierarchical structures with superhydrophilicity or superhydrophobicity. To fabricate regularly arrayed monolithic hierarchical structures, the UV-assisted replica molding and O_2 plasma etching methods were combined as illustrated in Figure 1. If the nanoscale roughness can be created on molded microstructures by O_2 plasma etching methods, the large-area production of regularly arrayed monolithic hierarchical structures would be possible. It has been reported that a surface roughness is increased when a hybrid material-containing organic polymer is etched by O_2 plasma under vacuum[32,39] owing to the O_2 plasma resistance of the inorganic-containing part.[32,39,40] These results indicate that the nanoscale roughness could be created, if organic polymers containing a etch-resistive material were etched by O_2 plasma. On the basis of these facts, we chose the Si-SSQA as an etch-resistive material to O_2 plasma, because the silsesquioxane acted as an etching barrier during O_2 plasma etching.[39,40] Among various acrylic monomers, the EGDMA with high Young's modulus (>4 GPa) was chosen as the main photocurable components to fabricate mechanically robust hierarchical structures.[33] As shown in Figure 1a, the Si-SSQA/EGDMA mixtures containing a photoinitiator were prepared as a roughness amplifying material during O_2 plasma etching. We expected that the Si-SSQA with low surface tension would be concentrated on the surface of the cured polymer mixtures[33] and act as a nanoscale etching barrier to O_2 plasma.

To investigate the ability of roughness amplification of the Si-SSQA/EGDMA mixtures during O_2 plasma etching, the flat samples composed of the Si-SSQA/acrylic mixtures were prepared on the glass substrate. The cured flat samples were treated with O_2 plasma as shown in Figure 2. The concentration of Si-SSQA and the O_2 plasma etching times were varied to investigate the degree of roughness amplification of the Si-SSQA/EGDMA mixtures. As expected, the nanoscale roughness with column-like shapes was created on the surface of the cured Si-SSQA/EGDMA mixtures after O_2 plasma exposure. The nanoscale roughness was very sharp at the low concentration of Si-SSQA. In addition, bundles containing several nanocolumns were clearly observed on etched surface when the O_2 plasma treatment time was increased and the concentration of Si-SSQA was decreased. By increasing the concentration of Si-SSQA in the photocurable mixtures, the nanoscale roughness with column-like shapes gradually disappeared.

The roughness of the nanocolumns on the Si-SSQA/EGDMA surface treated with O_2 plasma was further verified by AFM images (Figure 3). The roughness of pure EGDMA and pure Si-SSQA surfaces treated with O_2 plasma for 1 min was 4.2 and 1.2 nm, respectively (Supporting Information, Figure S1). On the other hand, the RMS roughness of O_2 plasma-treated samples composed of the Si-SSQA/EGDMA mixtures was varied from 32 nm to 2.16 μm and maximized

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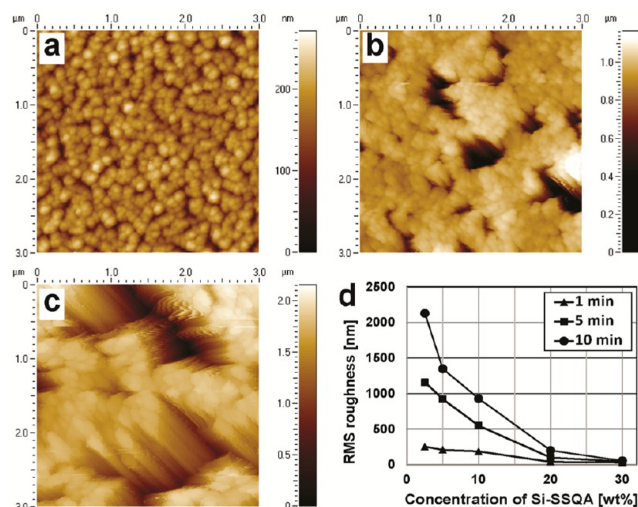

Figure 3. AFM image of cured EGDMA containing 2.5 wt % Si-SSQA after O_2 plasma etching for (a) 1 min, (b) 5 min, and (c) 10 min. (d) Variation of the RMS roughness on the surface as a function of Si-SSQA ratio after O_2 plasma treatment.

when the concentration of Si-SSQA was 2.5 wt % and the O_2 plasma etching time was increased. These results indicate that the Si-SSQA acts as an etching barrier during O_2 plasma treatment. In addition, these results suggest that the roughness of the cured Si-SSQA/EGDMA mixtures is efficiently controlled by varying the etching times and the weight ratio of Si-SSQA to acrylic monomer.

To fabricate regularly arrayed monolithic hierarchical structures, we fabricated the microstructures by UV-assisted replica molding as illustrated in Figure 1b. The first replicas with a convex microlens array pattern composed of the Si-SSQA/EGDMA mixtures were duplicated from the Si master with a concave microlens array patterns having the period of 1.44 μm and the height of 700 nm. The second replicas with the concave microlens array pattern composed of the Si-SSQA/acrylic mixtures were also fabricated by using same way. The microlens array patterns fabricated by UV-assisted replica molding were etched by O_2 plasma. As shown in Figure 4, the nanoscale roughness was successfully generated on the surface of the microlens patterns after O_2 plasma etching. The nanoroughness on microstructures was very clear at the low concentration of Si-SSQA. By increasing the Si-SSQA ratio, the nanoroughness on micropatterns was decreased and the plasma-etched micropatterns were similar to its original form. When the the O_2 plasma treatment time increased, the heights of the microstructures with nanoroughness increased, and the widths of microstructures decreased. The decrease of the widths of microstructures treated by O_2 plasma is closely related to the bundle formation of nanocolumns with a high aspect ratio because the high-aspect-ratio nanostructures with a low mechanical strength are not compliant as individual nanostructures.[41] These results suggest that geometrically controlled hierarchical structures composed of the Si-SSQA/acrylic mixtures could be fabricated over a large area by combining replica molding and O_2 plasma etching. The etching time was considered to obtain individual nanostructures on molded microstructures.

Wetting stability under long-term storage is an important attribute for wider implementation of products and devices that utilize superhydrophilic surfaces. To study the wetting stability,

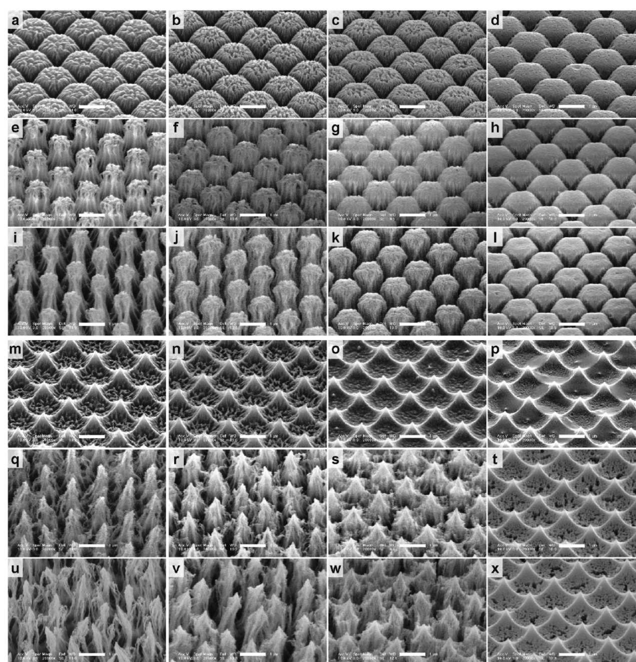

Figure 4. SEM images taken at a 45° tilt angle of (a−l) the first replicas and (m−x) the second replicas composed of the Si-SSQA/EGDMA mixtures after O_2 plasma etching for (a−d and m−p) 1 min, (e−h and q−t) 5 min, and (i−l and u−x) 10 min when the ratio of Si-SSQA was (a, e, i, m, q, u) 2.5 wt %, (b, f, j, n, r, v) 5 wt %, (c, g, k, o, s, w) 10 wt %, and (d, h, l, p, t, x) 30 wt %. The scale bar is 1 μm.

we treated the second replicas composed of the Si-SSQA/EGDMA mixtures with O_2 plasma. As shown in Figure 5a, the 30Si-SSQA/70EGDMA replica treated with O_2 plasma showed the WCA of 0°. In addition, the 30Si-SSQA/70EGDMA replica treated with O_2 plasma was maintained at 0° after 1 month of aging (Figure 5b). Furthermore, the O_2 plasma-treated all replicas shown in Figure 4 retained superhydrophilicity after 1

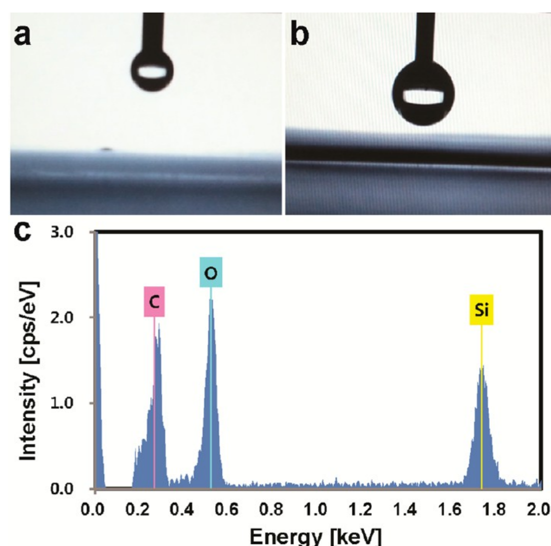

Figure 5. Photographs of water droplets on the 30Si-SSQA/70EGDMA replicas (a) after O_2 plasma etching and (b) after 1 month of aging. (c) EDXS spectra of the 1 month aged second replica composed of the 30Si-SSQA/70EGDMA mixtures after O_2 plasma treatment for 10 min.

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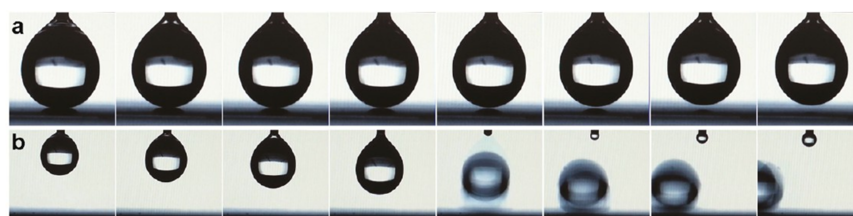

Figure 6. Snapshots of (a) the suctioning and (b) the falling of water droplets on the second replicas composed of the Si-SSQA/EGDMA mixtures after the O_2 plasma etching and the modification of PFOS SAM. The ratio of Si-SSQA was 5 wt %. The etching time was 5 min.

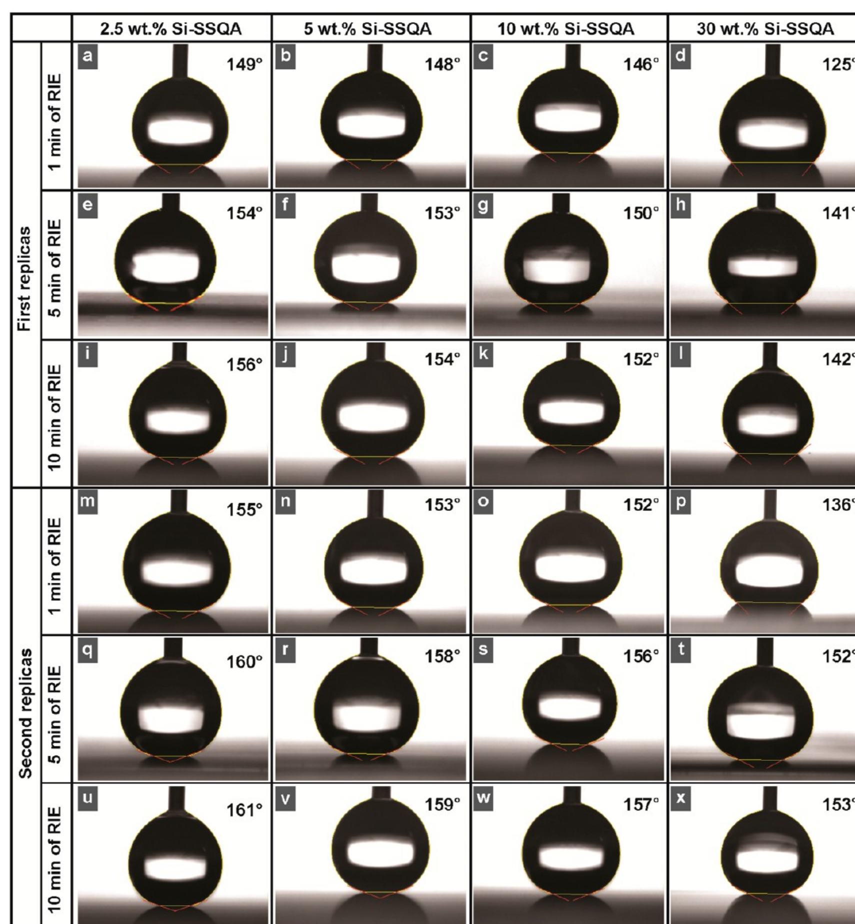

Figure 7. Photographs of a water droplet on (a−l) the first replicas and (m−x) the second replicas after the O_2 plasma etching and the modification of PFOS SAM. The etching time is (a−d and m−p) 1 min, (e−h and q−t) 5 min, and (i−l and u−x) 10 min. The ratio of Si-SSQA was (a, e, i, m, q, u) 2.5 wt %, (b, f, j, n, r, u) 5 wt %, (c, g, k, o, s, w) 10 wt %, and (d, h, l, p, t, x) 30 wt %.

month of aging (data not shown). The energy-dispersive X-ray spectroscopy (EDXS) data shows the existence of oxygen compounds on the surface of the O_2 plasma treated replica (Figure 5c). These results imply that an oxygen-related functionality, such as hydroxyl (OH) or carboxyl (COOH), and the silicon oxide (SiO_x), was generated on the surface of the cured Si-SSQA/EGDMA networks. In addition, these suggest that an oxygen-related functionality on the surface was not buried in the inside of cured networks. The super-hydrophilic long-term stability of the Si-SSQA/EGDMA networks treated with O_2 plasma is inconsistent with the polydimethylsiloxane (PDMS) treated with O_2 plasma in vacuum. It has been reported that the hydrophilic surfaces of PDMS treated with the O_2 plasma are unstable and undergo the hydrophobic recovery within a few hours,[42] because of the migration of the hydrophobic PDMS chains from the bulk PDMS to the surface of the OH-terminated SiO_x. This observation suggests that the hydrophobic silicone chain modified on the silsesquioxane acrylate could not migrate from the cured Si-SSQA/EGDMA networks to the surface of the OH-terminated SiO_x, unlike the PDMS case. It is thus concluded that the reorientation limit of the hydrophobic silicone chain from the cured networks to the OH-terminated SiO_x layer is the dominant factor for the long-term stability of superhydrophilicity.

The hierarchical structures composed of the Si-SSQA/acrylic mixtures were used to fabricate the superhydrophobic surface. For this purpose, the OH-terminated hierarchical structures fabricated by combining replica molding and O_2 plasma etching were modified with PFOS SAM. The wetting property of O_2 plasma-treated replicas modified with PFOS SAM was investigated by measuring the WCA. As shown in Figure 6,

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ACS Appl. Mater. Interfaces 2015, 7, 13490−13496

the hierarchically structured superhydrophobic replicas showed very low adhesion with the water droplets (Figure 6a) and caused water droplets bounce like a ball and rolled down the surface very quickly (Figure 6b). Therefore, the WCAs on the O_2 plasma-treated replicas modified with PFOS were measured by the captive droplet method to compare the wettability of hydrophobic and superhydrophobic surfaces.

Figure 7 shows the WCAs on the O_2 plasma-treated replicas modified with PFOS SAM. The WCAs on the O_2 plasma-treated replicas modified with PFOS SAM were controlled from 125 to 161°. The WCAs on the replicas modified with PFOS were increased by increasing the etching time and by decreasing the Si-SSQA ratio. The increments of the WCA by increasing the etching time and by decreasing the Si-SSQA ratio were consistent with the increment of the nano/microroughness (Figures 3 and 4). Meanwhile, the WCAs of second replicas with a sharp exterior surface were higher than that of corresponding first replicas with a blunt exterior surface. This result indicates that decrement of the top contact area of hierarchical structures played an important role for increment of WCAs. Therefore, it is expected that the wettability of hierarchical structures could be controlled by varying the size, shape, pitch, and height of the nano/microstructures.[43,44]

The mechanical and chemical stabilities of the hierarchical structure are important for the practical application of the superhydrophobic polymer surface. The minimum Young's moduli of Si-SSQA/EGDMA mixtures, at a contact depth between 30 and 200 nm, were controlled from 3 to 4.2 GPa by changing the ratio of Si-SSQA (Supporting Information, Figure S2). These high moduli would provide a high resistance to abrasion. In addition, the cured Si-SSQA/EGDMA mixtures exhibited high resistance to organic solvents (Supporting Information, Table S1). Furthermore, the hierarchically structured superhydrophobic replicas were transparent (Supporting Information, Figure S3). These results suggest that transparent hierarchical structures with the high mechanical and chemical stability can be fabricated by combining the replica molding and O_2 plasma etching methods.

■ CONCLUSION

In summary, we propose a simple method to prepare regularly arrayed hierarchical structures with superhydrophilicity or superhydrophobicity for large-area production. Liquid blends consisting of Si-SSQA and difunctional acrylics were developed as roughness amplifying materials during O_2 plasma etching and used as a material to fabricate microstructures. The microstructures composed of the Si-SSQA/acrylic mixtures were fabricated by UV-assisted replica molding method. The nanostructures (nanoroughness) were successfully created on molded microstructures by O_2 plasma etching. During the O_2 plasma etching processes, the Si-SSQA acted as an etching barrier. The nanoscale roughness on molded microstructures was effectively controlled by varying the weight ratio of Si-SSQA to acrylic monomer and the etching time. The hierarchical structures composed of the Si-SSQA/acrylic mixtures showed the superhydrophilic property with a long-term stability. This long-term stability was obtained by the formation of the OH-terminated SiO_x layer and the reorientation limit of the hydrophobic silicone chain modified on the silsesquioxane acrylate. Meanwhile, the hierarchical structures treated with perfluorinated SAM showed increased WCAs up to 161° depending on the nano/microroughness and the top contact area of hierarchical structures. It is thus anticipated that the combination of mold-based lithography and O_2 plasma etching will enable rapid, easy-to-implement and large-area production to fabricate regularly arrayed hierarchical structures with a superhydrophilic or superhydrophobic property for a wide range of applications.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details for measuring the mechanical property and swelling ratios, AFM height images of pure EGMDA and pure Si-SSQA after O_2 plasma etching, Young's modulus of cured Si-SSQA/EGDMA mixtures, optical image of hierarchical film after treatments of O_2 plasma and PFOS. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02673.

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Notes

The authors declare no competing financial interest.

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