

Fabrication of Superhydrophobic Surfaces by Self-Assembly and Their Water-Adhesion Properties

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The self-assembled films of methyloctyldimethoxysilane (MODMS) and fluorooctylmethyldimethoxysilane (FODMS) were prepared on silicon surfaces and evaluated with AFM, water contact angle measurement, and X-ray photoelectron spectroscopy. Superhydrophobic surfaces were obtained by cooperation of MODMS and FODMS self-assembly with surface roughening. The results showed that preparing closely packed self-assembled films and fabricating surface nanometer-scale and micrometer-scale binary roughness can achieve superhydrophobic films with a water contact angle larger than 156° . The difference between solution deposition and chemical vapor deposition is also investigated. Moreover, superhydrophobic surfaces created with MODMS and FODMS show the different water-adhesion effects, which could have great significance on liquid microtransport in microfluid devices.

Introduction

A superhydrophobic surface with a water contact angle (CA) larger than 150° has attracted much interest from both fundamental and practical aspects. It is well-known that wettability of a solid surface is governed by two dominant factors, which are surface composition and surface roughness. In general, a superhydrophobic surface can be prepared by combination of lowering the surface energy and enhancing the surface roughness.^{1–4} The self-assembly has been shown to provide a convenient route to prepare highly ordered and well-defined monolayer films.^{5–8} Among various self-assembled films, alkylsilane is promising for practical applications because of its marked mechanical and chemical stability due to the strong immobilization through siloxane bondings.^{9–12} Moreover, the self-assembly of alkylsilane is one of the efficient strategies to introduce low surface energy compounds on the surface to enhance surface hydrophobicity.^{13–16} The cooperation of alkylsilane self-assembly with surface roughening to realize superhydrophobicity has been reported.^{17–20} However, in the present paper, we report the preparation of superhydrophobic surface through combination of self-assembly of alkylsilane and its fluorinated analogue with a new surface roughening technology that is laser etching. Two kinds of self-assembly methods are used here, including solution deposition and chemical vapor deposition. The difference between them is investigated. The results indicate that fabricating closely packed assembled films and roughening the silicon surface with a laser-etching machine can achieve superhydrophobic surfaces with a water CA greater than 156° . In addition, the water-adhesion ability of the superhydrophobic surface created with alkylsilane by the solution deposition is different from that created by the chemical vapor deposition, which can be utilized to transport water droplets without loss.

Experimental Section

Materials. Methyloctyldimethoxysilane ($\text{CH}_3(\text{CH}_2)_7\text{Si}(\text{OCH}_3)_2\text{CH}_3$) (MODMS) and fluorooctylmethyldimethoxysilane ($\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_2\text{CH}_3$) (FODMS) were purchased from Fluka and Matrix Scientific, respectively, and used as received. The boiling points of MODMS and FODMS are 199°C and 80°C , respectively. 1,1,2-Trichloro-1,2,2-trifluoroethane (F-113) was obtained from Shanghai Chemical Reagent Co. and distilled with P_2O_5 before use.

The polished silicon wafers (100) (General Research Institute for Nonferrous Metals) were ultrasonicated in detergent solution and acetone for 30 min. After rinsed with water, the samples were submerged in a freshly prepared mixture of H_2SO_4 (98%) and H_2O_2 (30%) at a volume ratio of 7: 3. The solution was heated to 80°C for 1 h to remove organic contaminants. Then, the samples were rinsed thoroughly with Milli-Q water and dried with a N_2 gas stream. After such treatments, a thin oxide layer formed on the silicon surface.

Roughening of Silicon Surface. The roughening of silicon surface was realized with QuikLazeII Laser etching machine (New Wave Research, U.S.). The laser pulse was UV light and the repetition rate was 20 Hz. The laser pulse dredged grooves in micrometer scale on silicon surface to form different regular patterns. By adjusting the size of the laser spot and the intensity of the laser pulse, the width and depth of the microgrooves could be altered.

Reaction of Silicon Surface in Solution. The 10 mL 50 mM freshly prepared silane precursor solutions in F-113 were pipetted to a glass container and the silicon surfaces were covered with the solution. Reaction was run at 47°C (F-113 boiling point) at a deposition time ranging from 10 min to 4 h. Then, modified substrates were ultrasonicated for 5 min, rinsed with fresh F-113, and dried under a flow of N_2 . Finally, the modified substrates were treated thermally in an oven at 150°C for 2 h.

Chemical Vapor Deposition on Silicon Surface. The substrates were placed in a 50-mL sealed vessel with a container

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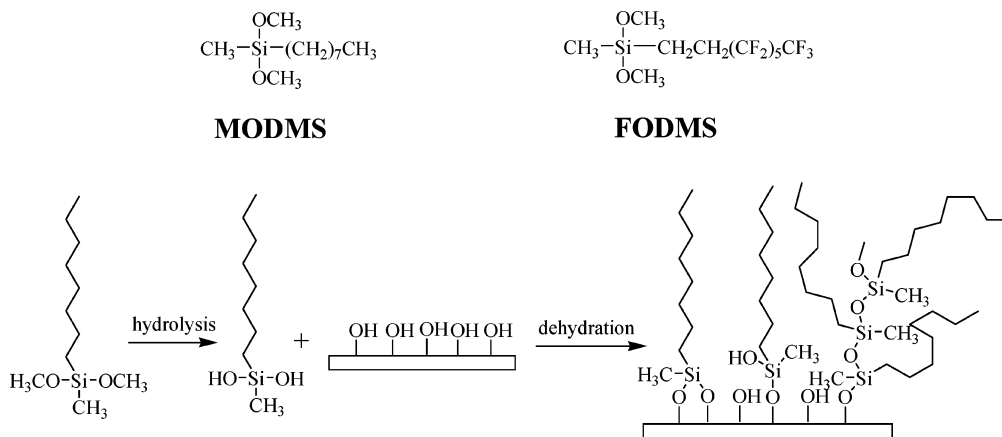


Figure 1. Chemical structures of alkylsilanes and the formation scheme of self-assembled film on hydrated silicon surface.

filled with 0.2 mL silane precursor liquid. There was no direct contact between the liquid and the substrates. The vessel was put in an oven maintained at 150 °C for 3 or 6 h. As the boiling point of MODMS is higher, more time is required for self-assembly process of MODMS than that of FODMS. The precursor vaporized and reacted with the OH groups of surface, resulting in the formation of self-assembled films. Then, the substrates were ultrasonicated for 5 min in F-113, rinsed with F-113, and dried under a flow of N₂.

Surface Characterization. The water contact angle (CA) was measured with a 5-μL water droplet at ambient temperature with an optical contact angle meter (Dataphysics Inc, OCA20). Expanding and reducing the volume of water droplet on a horizontal surface could obtain advancing and receding water contact angles. Then, the contact angle hysteresis can be determined from the difference between the advancing and receding contact angles. The CA values reported are averages of five measurements made on different areas of the sample surface. All measurements for all surfaces were within ±2.0° of the averages. Morphology of the sample surfaces was observed with AFM (Digital Instruments, Nanoscope III A, tapping mode) and field-emission scanning electron microscopy (SEM, JEOL JSM-6700F, Japan). The composition of the treated surfaces was studied by X-ray photoelectron spectroscopy (VG ESCALAB MKII spectrometer) with an AlK_α monochromatic X-ray source.

Results and Discussion

First, the self-assembly of alkylsilane has been carried out on smooth silicon surfaces. Methyloctyldimethoxysilane (MODMS) is assembled on smooth silicon surfaces through solution deposition using 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) as a solvent at a deposition time ranging from 10 min to 4 h. To remove excess MODMS aggregates, the samples are ultrasonicated with F-113 for 5 min. To compare the wettability between alkylsilane and its fluorinated analogous, smooth hydrated silicon surfaces are also modified with fluorooctyldimethoxysilane (FODMS). The chemical structures of alkylsilanes and the self-assembly process are shown in Figure 1. As reported,^{5,13,14} reactive difunctional alkylsilanes (R₂SiX₂) with hydrolyzable groups (X = Cl, OR, NMe₂) are able to hydrolyze at the hydroxylic substrate surface to generate a silanol, which can react with -OH groups on the oxide surface, resulting in the formation of a self-assembled film. Meanwhile, the surface also can induce vertical polymerization to form grafted polysiloxane. Consequently, MODMS and FODMS molecules are covalently attached and the nanometer-scale aggregates are generated through the vertical polymerization.

The morphology of silicon surfaces modified with MODMS is shown in Figure 2. It is obvious that short-time deposition of ca. 10 min gets smooth surfaces (Figure 2A). When the deposition time exceeds 2 h, the formation of surface aggregates with the height of about 4 nm can be observed (Figure 2B). As deposition time increases to 4 h, the amount of the aggregates appears to be growing and the height reaches ca. 6 nm (Figure 2C). That is to say, the morphology of the self-assembled films can be controlled by deposition time. Hence, the wettability of the self-assembled films is influenced from weak hydrophilicity (CA = 59.4°) to weak hydrophobicity (CA = 87.1°). It is possible that the coverage of alkylsilane is lower at short deposition time, while it will be raised during the long-time self-assembly, which can provide higher quality surfaces modified with low surface energy compounds.

The composition of the self-assembled surface is studied with X-ray photoelectron spectroscopy (XPS). Figure 2D shows the C 1s spectrum of the smooth silicon surface modified by MODMS. The single peak centered at 284.6 eV supports the idea that self-assembly has successfully introduced hydrophobic groups to the silicon surfaces.

The smooth surface modified with MODMS exhibits water CA slightly lower than the reported value for silicon surfaces treated with methyloctyldichlorosilane¹⁴ and octyltrimethoxysilane.²¹ The smooth surface modified with FODMS shows a water CA of 93.8°, close to the water CA reported by Yoshino et al.¹⁶ Considering that the difunctional precursor will polymerize in solution, and the oligomeric precursors can also react with the silanol and covalently attach to the silicon surface, the self-assembled films are less ordered and water can penetrate into the self-assembled film so as to lower the hydrophobicity.¹⁴ To eliminate the impact of oligomeric precursors, the self-assembled films of MODMS and FODMS are also performed on smooth silicon surfaces through chemical vapor deposition. During this procedure, the oligomeric precursors in solution have lower vapor pressure and are rarely vaporized. Therefore, through vapor-phase deposition process, the deposition of oligomeric precursors can be eliminated,^{10,22} while the as-prepared self-assembled film will be more ordered and closely packed and the coverage of precursors will be higher. As shown in Figure 3, the modified silicon surfaces appear to be smoother than those taken from alkylsilanes solutions. The hydrophobicity of modified surfaces formed at the vapor/solid interface is superior to that of the films prepared by solution deposition, showing water CA of 93.2° for MODMS surface and 106.5° for FODMS surface. It means that ordered and closely packed self-assembled films can be fabricated through chemical vapor

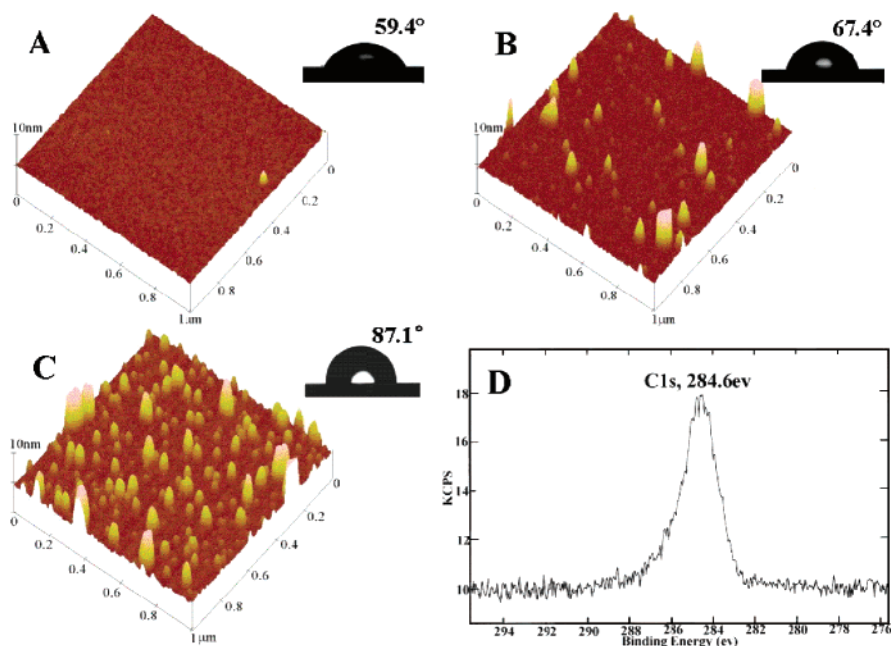


Figure 2. The 3D AFM images of MODMS self-assembled films on smooth silicon surfaces (A) after 10-min deposition, (B) after 2 h, (C) after 4 h, (D) XPS C 1s spectrum of smooth silicon surface modified with MODMS after 4 h. The insets show the profile of water droplets on the surfaces and water CA.

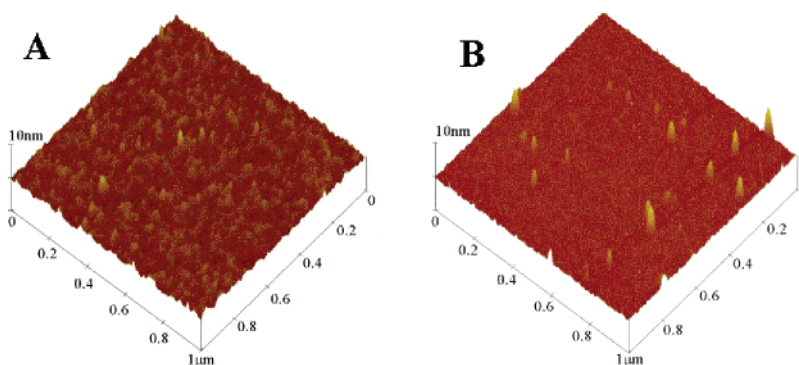


Figure 3. The 3D AFM images of self-assembled films on smooth silicon surfaces through chemical vapor deposition. (A) Modified with MODMS, (B) modified with FODMS.

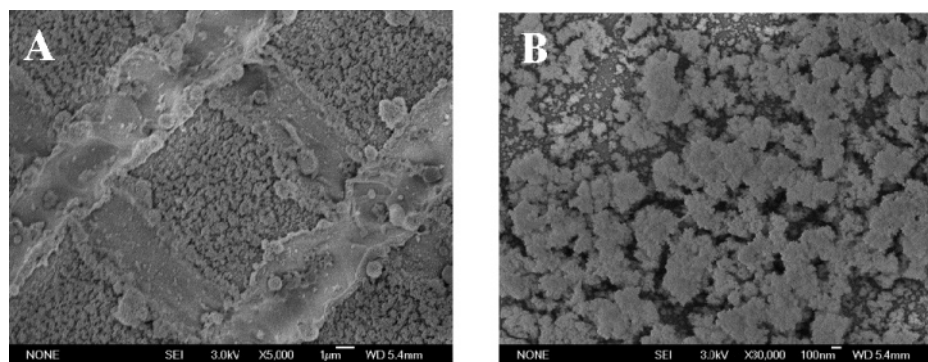


Figure 4. SEM images of etched silicon surfaces with laser-etching machine without modification. (A) Rough surface, (B) magnified image of the microconvex.

deposition and the hydrophobicity of self-assembled films is also improved.

To prepare superhydrophobic surfaces, the cooperation of low surface energy and surface roughness is realized by coating MODMS and FODMS, respectively, on laser-etched rough silicon surfaces. The size of the pattern is chosen according to the previous work.³ Figure 4 A shows an SEM image of silicon surface roughened with the laser-etching machine. The rough surface exhibits vertically intersecting micrometer-scale grooves,

which are generated with laser etching with ca. 5 μm in depth and 4 μm in width. Between every two microgrooves, micrometer-scale convexes are generated. The convexes are ca. 7 μm in width. The magnified SEM image of the microconvexes (Figure 4B) shows that the microconvexes consist of many nanometer-scale particles and pores, which are generated during laser etching. The laser-etching machine dredges grooves on silicon surface; meanwhile, the sputtered chippings are oxidized into SiO₂ and stack on the adjacent convexes. In this way, nanom-

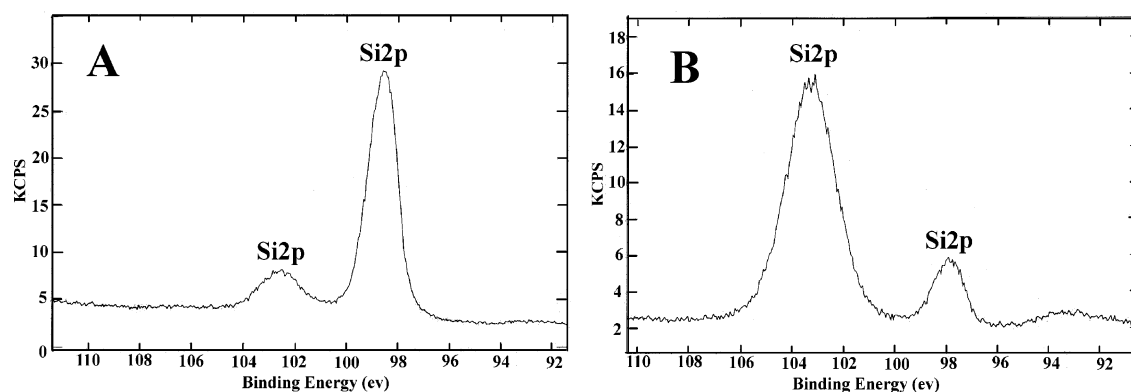


Figure 5. XPS Si 2p spectra of silicon surfaces without modification. (A) Smooth silicon surface, (B) rough silicon surface.

TABLE 1: Values of Water Contact Angle in Degrees for Modified Silicon Surfaces by Solution Deposition and Chemical Vapor Deposition

water CA	MODMS solution (°)	MODMS vapor (°)	FODMS solution (°)	FODMS vapor (°)
smooth	87.1	93.2	93.8	106.5
rough	156.7	>160.2	158.2	>165.0

eter-scale protuberances and pores are formed. Compared with modified smooth silicon surfaces, the hydrophobicity of modified rough ones is improved significantly, as shown in Table 1. Using solution deposition, the water CA of the rough surface increases to 156.7° for MODMS and to 158.2° for FODMS. Using vapor-phase deposition, the water CA of the rough one increases to >160.2° for MODMS and >165.0° for FODMS. Because water droplets are very unstable on the superhydrophobic surfaces modified through chemical vapor deposition, the water CA of these surfaces cannot be decided precisely. According to Cassie's model, the nanometer-scale and micrometer-scale binary roughness fabricated with laser etching intensifies the proportion of air trapped in pores and contributes to the formation of superhydrophobic surfaces.^{23–26}

Figure 5A and B presents the Si 2p spectra of the smooth and rough silicon surfaces without modification. Both of the spectra consist of two peaks, which correspond to Si–Si at 98.6 eV (Si1) and Si–O at 103.4 eV (Si2), respectively. The Si1 signal intensity of the smooth surface is much larger than that of the rough surface, which in reverse for the Si2 signal intensity. These results indicate that the amount of SiO₂ on the silicon surface is improved and a thicker SiO₂ layer is generated during laser etching. This oxide layer enlarges the number of –OH groups exposed on the surfaces and then increases the reacted MODMS and FODMS amounts, which in turn enlarges water CA to some extent.

Under the two different methods in solution and in vapor deposition, rough silicon surfaces modified with alkylsilanes are all superhydrophobic; however, the situation of the water droplet on them is totally different. No matter what kind of precursor is self-assembled, water droplets move spontaneously on the modified surfaces through chemical vapor deposition and hardly come to rest on horizontal surface. The roll-off behavior is recorded with a high-speed photography as shown in Figure 6A, and the water droplet is 5 μ L, equal to that used to measure the contact angle. The sliding angle is close to 0°. However, water droplets will bead up and adhere to the surfaces modified through solution deposition. Water droplets cannot roll off until FODMS surface is tilted to 18.5°. When the MODMS surface is tilted to any angle, even upside down, the droplet stays pinned to the surface (Figure 6B). That is to say, the superhydrophobic silicon surfaces modified in solution provide higher adhesion to water, while the surfaces modified in chemical vapor deposition show little adhesion to water.

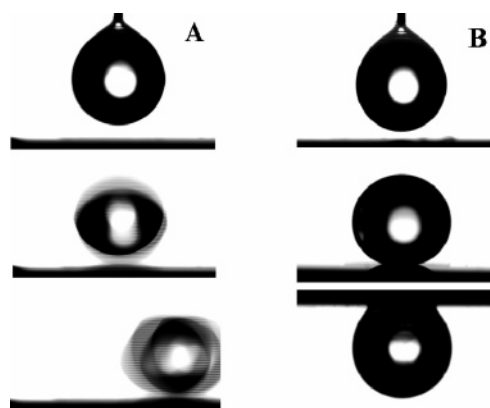


Figure 6. The behavior of water droplets on the modified silicon surfaces, which are etched with laser-etching machine and modified with (A) FODMS and MODMS self-assembled film through chemical vapor deposition, (B) MODMS self-assembled film through solution deposition. The water droplet is 5 μ L.

The relationship between the contact angle hysteresis and the force applied for the water droplet to move on hydrophobic surface had been discussed by Öner and McCarthy.²⁶ The contact angle hysteresis is most often ascribed to surface roughness, chemical heterogeneity, and the reorientation of functional surface groups occurring in contact with liquid.^{27,28} To better understand the different behavior of water droplet on surface, the values of the contact angle hysteresis of these superhydrophobic surfaces have been measured as well and they are all smaller than 4°. Therefore, these superhydrophobic surfaces should be chemical homogeneous, and the different behavior of water droplet on these surfaces could not be explained just by contact angle hysteresis.

Because the deposition of oligomeric precursor has been eliminated in chemical vapor deposition, the surfaces self-assembled in vapor phase are more closely packed and more hydrophobic. Combination with the surface roughening, silicon surfaces modified with MODMS and FODMS both show little adhesion to water. As a result, the static CA for the superhydrophobic surfaces modified with FODMS (>165.0°) and MODMS (>160.2°) are both pretty large and the sliding angle is close to 0°. Moreover, owing to the polymerization of precursor in solution, the self-assembled film in solution is less ordered than in vapor phase. There may exist trace hydrophilic silanol groups on the film assembled through solution deposition.

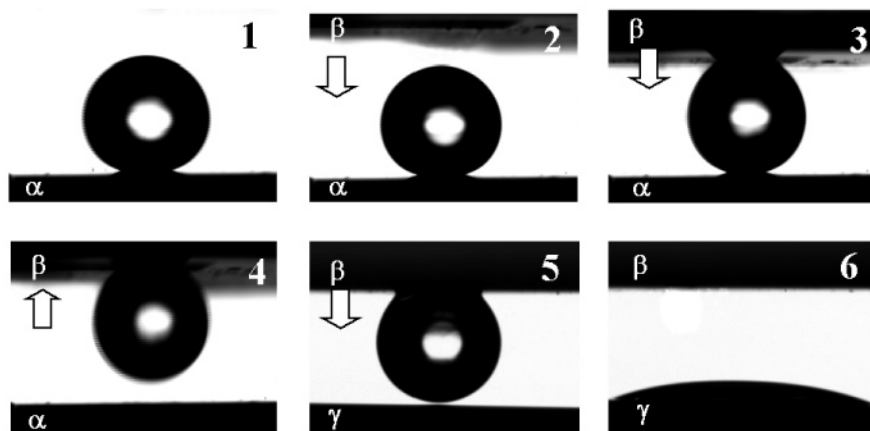


Figure 7. The process of transporting the water droplet. The surfaces α , β , and γ are silicon surface modified with FODMS in solution deposition, silicon surface modified with MODMS in solution deposition, and hydrophilic silicon surface, respectively.

It is possible that the film assembled through solution deposition is a composite one with hydrophobic alkyl groups and trace hydrophilic silanol groups. The alkyl groups can lower the surface energy greatly; however, the silanol groups may stick water. Therefore, the surface fabricated in solution has a strong adhesion to water, though the water CA is pretty large. As for the fluorinated surface, the lower polarizability of fluorine than hydrogen leads to very weak van der Waals interactions among the fluorinated chains and between the fluorinated chains and polar molecules of water.^{29–31} Thus, the surfaces fluorinated in solution are more hydrophobic than that coated with MODMS, and the sliding angle of FODMS surface (18.5°) is smaller than MODMS surface (180°).

The difference of water adhesion effects mentioned above can be used to carry out water transport. A water transport experiment has been done and the process is shown in Figure 7. First, a $5\text{-}\mu\text{L}$ water droplet was carefully put on the FODMS modified surface because of its instability (step 1). Then, MODMS surface modified in solution deposition was lowered to contact the water droplet (steps 2, 3). Because of the strong adhesion force between the MODMS modified surface and water, the water droplet can bead up and adhere to the MODMS surface completely (step 4). Finally, the adsorbed water droplet on the MODMS modified surface can be transported to a hydrophilic silicon surface by touching (steps 5, 6). Thus, the water transport among superhydrophobic surfaces and hydrophilic surfaces is realized by the adhesion effect.

Conclusions

In summary, the self-assembled films on silicon surfaces with MODMS and FODMS are prepared by solution deposition and chemical vapor deposition. These two different self-assembly methods are evaluated according to the hydrophobicity and morphology of modified surfaces. There may exist the deposition of oligomeric precursors in solution. Self-assembly in vapor/solid interface can eliminate this shortcoming. It can be concluded that a superhydrophobic surface can be achieved through a cooperation of two factors: one is closely packed and thick self-assembled film of low surface energy compounds; the other is micrometer- and nanometer-scale binary roughness. Furthermore, the superhydrophobic surface coated with MODMS in solution provides high adhesion to water and the superhydrophobic surface coated with FODMS almost has little adhesion to water. This special wettability may have great significance on liquid microtransport in microfluid devices.

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