Superhydrophobic CF$_x$ Coating via In-Line Atmospheric RF Plasma of He–CF$_4$–H$_2$

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Stable superhydrophobic coatings on various substrates are attained with an in-line atmospheric rf plasma process using CF$_x$, H$_2$, and He. The coating layer is composed of CF$_x$ nanoparticulates and has an average roughness of ~10 nm. This roughness is much smaller than other surfaces reported for superhydrophobicity in the literature. The superhydrophobic coatings are produced on both metallic and insulating substrates without any need of separate microroughening or vacuum lines.

Introduction

Superhydrophobic surface treatments of various substrates are of great interest in recent years. A superhydrophobic surface has a water contact angle higher than 150° and very low contact angle hysteresis. On these surfaces, water droplets do not wet the surface at all and easily roll off removing dirt and debris. An example in nature is the lotus leaf. It is known that chemical modification of artificial materials using fluoropolymers or silane layers cannot give water contact angles higher than 120°. To reach the extreme values of the contact angle near 150°, surface roughness is often added to amplify the hydrophobicity of the coating materials. The surface topography effects have been mathematically described by the Wenzel equation and the Cassie–Baxter equation. On the basis of these principles, synthetic superhydrophobic surfaces have been fabricated by creating rough surface morphology covered with low surface energy molecules. Most of these methods are applicable only to specific substrate surfaces; in general, a broad applicability is lacking. The lower limit of the surface roughness to attain the superhydrophobicity is not unambiguously determined yet. Among many techniques that can be utilized for hydrophobic and superhydrophobic treatments, plasma-based processes have been widely studied and developed. The plasma-based treatment methods provide advantages of no liquid waste generation and a high efficiency of surface activation by dual actions of radicals and charged particles (electrons and ions). However, the practical application of plasma-based processes has been hampered due to the following reasons. A majority of the plasma-based processes developed so far are vacuum plasma; so they are not suitable for continuous in-line manufacturing. In the batch process, the sample transfer into and out of a vacuum system is quite inconvenient and slow. There are several examples of atmospheric plasma processes demonstrated, but the plasma stability, low power operation, and/or large area treatments still remain as challenges that need to be solved for practical applications.

This paper demonstrates a simple and manufacturable method for formation of superhydrophobic coatings on a wide range of substrates. The superhydrophobic coating is produced by an in-line atmospheric radio frequency (rf) plasma process.

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H₂, and He gases. The surface roughness of the produced samples with a diameter of 10 cm is only 1–2 min.

**Experimental Section**

The atmospheric rf glow-discharge plasma system was constructed with a custom-made plasma generator head and a 13.56 MHz rf supply with a L–C matching unit. A schematic of the plasma head and sample stage is shown in Figure 1. The plasma discharge characteristics are similar to the one reported in ref 27. Helium was used as a carrier gas (5–10 lpm) and a mixture of CF₄ and H₂ was used as a reactive gas (20–80 sccm). The rf power was controlled in the range of 300–400 W. The effective plasma area was 1 cm wide and 16 cm long. Since the plasma was operated in a glow discharge mode, it could be directly applied to metallic substrates as well as nonconductive surfaces without arc or streamer damage. Samples were traveled about 0.5 cm below the plasma source along the plasma width direction. In typical processes, the substrate was repeatedly traveled back and forth across the glow-discharge plasma region at a speed of 1 cm/s. The substrates tested in this work were clean Si wafers, gold films deposited on Si wafers, glass slides, Kimwipe papers, and cottons with 20 thread counts per centimeter. Si, gold, and glass samples were cleaned with an oxygen plasma prior to hydrophobic treatments.

In the atmospheric CF₄–H₂–Ar plasma treatment for superhydrophobic coating, the two most important parameters were the speed at which the sample was moved under the plasma head and the use of hydrogen. When the plasma treatment speed was decreased lower than 0.5 cm/s, we could not attain the superhydrophobicity at all. The deposited coating showed only mild hydrophobicity and assumed some burn color. When the speed was increased faster than 2 cm/s, we needed more cycles since only one side of the Kimwipe paper and cotton surfaces, water was completely absorbed. The contact angle did not change noticeably for samples treated with one pass. Samples treated 3 times with the plasma showed 173°. The variation in water droplet coalescence. Dynamic behavior of water on the plasma-deposited superhydrophobic coating was tested with a high-speed camera (Photron, Ultra APX RS) at a 3000 Hz frame rate. Chemical analyses of the superhydrophobic coating were performed with polarization-modulation reflection–absorption infrared spectroscopy (PM-RIRS) and X-ray photoelectron spectroscopy (XPS). PM-RIRS spectra were acquired with Thermo Nicolet NEXUS 670 and HINDS photoelastic modulation units. XPS analysis was performed with two different instruments, VG ESCALAB MK-II and Kratos Analytical Axis Ultra. The Kratos instrument was equipped with a charge compensation electron flood gun. The XPS data from these two instruments were compared to check differential charging of the sample. The topography of the deposited film was imaged with tapping-mode atomic force microscopy (AFM) composed with a Molecular Imaging Pico-SPM scanner with a RHK controller unit. An ultrasharp Si tip (MikroMash) was used for imaging. The resonance frequency was 200.7 kHz, and the free-standing amplitude was 1.4 nm. The tapping scanning was made with a 10% damping of the amplitude.

**Results and Discussion**

Regardless of the substrate nature, all samples treated with the CF₄−H₂−He atmospheric rf plasma for more than 5 passes showed superhydrophobicity. After 10 passes, the success rate reaches 100%. Before the plasma treatment, water contact angles on clean Si wafer, gold film, and glass substrates were less than 5°. On Kimwipe paper and cotton surfaces, water was completely absorbed. The contact angle did not change noticeably for samples treated with one pass. Samples treated 3 times with the plasma showed 173°. The variation in water droplet coalescence. Dynamic behavior of water on the plasma-deposited superhydrophobic coating was tested with a high-speed camera (Photron, Ultra APX RS) at a 3000 Hz frame rate. Chemical analyses of the superhydrophobic coating were performed with polarization-modulation reflection–absorption infrared spectroscopy (PM-RIRS) and X-ray photoelectron spectroscopy (XPS). PM-RIRS spectra were acquired with Thermo Nicolet NEXUS 670 and HINDS photoelastic modulation units. XPS analysis was performed with two different instruments, VG ESCALAB MK-II and Kratos Analytical Axis Ultra. The Kratos instrument was equipped with a charge compensation electron flood gun. The XPS data from these two instruments were compared to check differential charging of the sample. The topography of the deposited film was imaged with tapping-mode atomic force microscopy (AFM) composed with a Molecular Imaging Pico-SPM scanner with a RHK controller unit. An ultrasharp Si tip (MikroMash) was used for imaging. The resonance frequency was 200.7 kHz, and the free-standing amplitude was 1.4 nm. The tapping scanning was made with a 10% damping of the amplitude.

![Figure 1](image1.png)

**Figure 1.** Cross-section view of the atmospheric rf glow-discharge plasma head and sample translation stage.

![Figure 2](image2.png)

**Figure 2.** (a) Photograph image of water droplets (~2 mm diameter) on a superhydrophobic coating deposited on (a) gold film, (b) Si wafer, (c) Kimwipe, and (d) cotton.
samples was treated with the plasma, the untreated side readily absorbed water droplets.

The ESEM analysis of water condensation and water droplet coalescence reveals the wetting behavior on a microscopic level [data presented in the Supporting Information]. All microdroplets condensed on the CF$_4$–H$_2$–He plasma-treated Au film substrates are completely spherical. Even though these droplets are separated by less than 1 μm, they do not coalesce, indicating the highly nonwetting nature of the surface. When the surface is not superhydrophobic, droplets coalesce before they grow to get this close.

Dynamic behavior of water on the plasma-deposited superhydrophobic coating is tested with water droplet free-falling on the coating. Figure 3 shows selected time sequence images taken with a high-speed camera at a 3000 Hz frame rate [full video clips available in the Supporting Information]. Upon landing on the superhydrophobic coating surface, the water droplet advances (panels 3 and 4) and then recedes (panels 5 and 6) with a contact angle greater than 90°. The actual contact angle is estimated to be close to 170°, same as the static measurement values, from the image of water droplet just at the bouncing-off moment. At this high contact angle, the three-phase (solid–liquid–air) contact line does not propagate outward from the center of the contact region. Since the contact line circumference is so small, the momentum loss due to liquid surface tension at the contact line is negligible and the droplet bounces back off the surface almost elastically (panels 7 and 8). Upon recoiling from a flat substrate, the water droplet shows a symmetric bubble oscillation behavior. On the CF$_4$–H$_2$–He plasma treated cotton surface, the water droplet bounces off with an irregular shape due to the macroscopic roughness of the cotton fabric. On hydrophilic surfaces (Figure 3b), the water droplet spreads with a very low contact angle and never recedes back. On the untreated cotton surface (Figure 3d), the water droplet advances with a contact

angle greater than the hydrophobic flat surfaces, but does not recede. The water is eventually absorbed into the cotton.

The chemical functional groups in the superhydrophobic coatings deposited via the atmospheric rf glow-discharge plasma process are identified with PM-RAIRS. Figure 4 displays PM-RAIRS data of a gold substrate processed with the atmospheric CF4−H2−He plasma for increasing the number of passes. Main peaks are the C−F stretching vibrations at 1245, 1285, and 1348 cm−1 and the C−O stretching vibration at 1730 cm−1. A poly(tetrafluoroethylene) (PTFE) reference sample gives two well-resolved peaks at 1205 and 1150 cm−1 for asymmetric and symmetric CF2 stretching vibrations, respectively (data not shown). The fact that C−F and C−O vibrations of the coating are broad and not well resolved indicates that the coated material is amorphous and highly cross-linked. Other vibrational peaks found in PM-RAIRS include nitrile at 2280 cm−1, C−H at 2985 cm−1, N−H at 3400 cm−1, and O−H at 3620 cm−1. However, their concentrations are negligible compared to the C−F groups.

The chemical composition of the superhydrophobic coating is obtained from XPS analysis. Figure 5 shows a survey spectrum of a 3-pass coating on a gold film, and Table 1 reports the summary of the elemental analysis. The main components in the coating are carbon and fluorine. There are trace amounts of nitrogen and oxygen detected. These species are incorporated because the plasma is generated in air. Although the C=O peak in PM-RAIRS seems quite large, the actual concentration of oxygenated species is only ~3%. It should be noted that the C=O vibration has the highest sensitivity in IR. The fluorine-to-carbon ratio is ~0.6 for samples treated 3 times and decreases further to ~0.4 for samples treated more than 5 times. The high-resolution C1s region shows 4 different carbon species (Figure 5 inset). The peak at 285 eV is attributed to C−C species. In the XPS handbook,29 the peak at 287.2 eV can be assigned to C−F and C=O. The 289.8 and 292.4 eV peaks correspond to CF species adjacent to CF2 and PTFE-like CF2−CF2 species, respectively. On the basis of these XPS data, the chemical composition of the superhydrophobic coating is represented as CFx (x < 1).

There are several features in XPS data implying that the CFx superhydrophobic coating is composed of particulates. The Au substrate peak is still detectable even after 12 passes of the plasma deposition process. This indicates that there are still small amounts of bare gold surface regions that are not covered with the CFx coating. In high resolution spectra, the gold peaks are not shifted at all due to charging, whereas the C1s and F1s peaks are significantly shifted. For the 3-pass treated sample, the full-width-half-maximum of the C1s peak of the CFx coating is ~1 eV larger than that of PTFE. The C1s and F1s peaks get broader as the number of plasma deposition increases. These are due to differential charging of the sample in XPS measurements. The differential charging is observed for samples consisting of nonconducting domains with varying thickness and incomplete coverage on a conducting substrate. In this case, the kinetic energy of photoelectrons from different locations of the nonconducting domains varies depending on the degree of charging of the location from which they are generated. This kind of peak broadening is not observed for homogeneously deposited films or PTFE reference samples.

Table 1. Concentration of Elements Detected in XPS (in atom %)

<table>
<thead>
<tr>
<th>sample</th>
<th>Au</th>
<th>C</th>
<th>F</th>
<th>N</th>
<th>O</th>
<th>F/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 passes</td>
<td>10.3</td>
<td>51.7</td>
<td>32.3</td>
<td>2.4</td>
<td>3.3</td>
<td>0.62</td>
</tr>
<tr>
<td>7 passes</td>
<td>4.9</td>
<td>65.3</td>
<td>25.5</td>
<td>2.0</td>
<td>2.4</td>
<td>0.39</td>
</tr>
<tr>
<td>12 passes</td>
<td>1.2</td>
<td>68.3</td>
<td>26.1</td>
<td>1.5</td>
<td>3.0</td>
<td>0.38</td>
</tr>
<tr>
<td>PTFE standard</td>
<td>0.0</td>
<td>33.2</td>
<td>66.8</td>
<td>0.0</td>
<td>0.0</td>
<td>2.01</td>
</tr>
</tbody>
</table>


Figure 6. 750 nm × 750 nm AFM images of a gold film substrate treated with the CF4−H2−He atmospheric rf glow-discharge plasma for (a) 0, (b) 3, (c) 7, and (d) 11 times. The full contrast scale of each image is (a) 14.4 nm, (b) 44.6 nm, (c) 64.0 nm, and (d) 79.6 nm.

Figure 7. Distribution of topographic heights of AFM images shown in Figure 6. The integrated area of each curve is normalized to 100%.
The accurate topography of the superhydrophobic CF₄ coating was revealed from AFM imaging. Figure 6 shows a series of tapping-mode AFM images of a gold film substrate as a function of the plasma treatment passes. After treatment with the CF₄–H₂–He plasma three times, one or two big particulates with a height of ~40 nm and a diameter of ~200 nm are observed in a 750 nm × 750 nm area. The number of these large particulates increases as the number of plasma deposition increases. The tallest feature height also increases to 64 nm for 7 passes and 77 nm for 11 passes. Figure 7 plots the height distribution of the images shown in Figure 6. The average roughness over a 750 nm × 750 nm increases from 2.2 nm for the untreated gold film (base substrate) to 7.2 nm for 3 passes, 11.8 nm for 7 passes, and 16.8 nm for 11 passes. The average height also increases from 8.5 nm for the base substrate to 15.2 nm for 5 passes, 26.8 nm for 7 passes, and 34.5 nm for 11 passes.

The XPS and AFM results indicate that the superhydrophobic coating consists mostly of CF₄ nanoparticulates. Particulate formation is known to occur at relatively high density of reactive radicals and ions in the plasma. Under these conditions, diffusion path lengths of reactive species are very short, and gas-phase reactions take place. Upon reaching a critical number density, rapid condensation of the gas-phase species is triggered, resulting in particulate deposition onto the substrate. When the CF₄ flow rate is lowered to <5 sccm, the treated substrate does not exhibit superhydrophobicity. Due to low CF₄ concentration in the plasma, the CF₄ nanoparticulates are not produced.

The remarkable feature of this atmospheric rf plasma deposition of CF₄ coatings is that the superhydrophobicity is attained with a low aspect ratio (height/diameter < 0.2) and an order of 10 nm height scale. Most of the superhydrophobic surfaces reported in the literature have aspect ratios larger than 1 and feature sizes larger than 100 nm. To the best of our knowledge, the roughness of the superhydrophobic coatings produced by this atmospheric CF₄–H₂ rf plasma is the smallest among similar kinds. Most of current theories based on continuum models focus on the shape of the surface topographic feature but not on the size scale. A recent theory derived by Marmur predicts a critical aspect ratio of the topographic features to render the superhydrophobicity. However, the aspect ratio of the plasma-deposited particulates is lower than the predicted critical value. The continuum theory predicts that the highest contact angle on the flat surface does not exceed 120°. In reality, there is no perfectly flat surface in the molecular level. The 10 nm roughness scale is only 2 orders of magnitude larger than the molecule size, which is typically assumed to be smooth in other applications. The prediction of the minimum roughness for superhydrophobicity may require multiscale theoretical studies combining quantum mechanics and continuum theories of surface tension forces.

Another important aspect is that the atmospheric rf glow-discharge plasma can be applied to any surfaces regardless of the surface chemistry of the substrate—metals, metal oxides, Kimwipe papers, cottons, etc. Because of this versatility of applicable substrates, this plasma process can be utilized in a wide range of applications such as self-cleaning fabrics, planar microfluidics, corrosion and adhesion protections, etc. The roughness of the underlying substrates is not an important factor in this plasma treatment. Unlike other methods, this method does not require any pretreatment of the substrate for roughening of the substrate surface. The CF₄ superhydrophobic coating is very stable and durable as long as there is no severe mechanical abrasion. There is no noticeable degradation of the superhydrophobicity for the samples exposed in air for long periods of time (we tested up to 4 months). The coating on cotton fabric does not degrade even after many cycles of cold water wash (without mechanical rubbing).

## Conclusion

We have demonstrated the formation of superhydrophobic coatings via atmospheric rf glow-discharge plasma treatments using CF₄, H₂, and He. The coating has a chemical composition of CF₄ (x < 1). The topographic features of the CF₄ coating have aspect ratios less than 1 and are not taller than a few tens of nanometers. This approach provides a simple process for making superhydrophobic coatings on various substrates without any pretreatments for surface roughening.

## Acknowledgment

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## Supporting Information Available

Videos of dynamic water drop falling tests on uncoated and coated Si wafer and cotton samples; ESEM images of condensed water droplets on superhydrophobic and hydrophilic substrates. These are available free of charge via the Internet at http://pubs.acs.org.

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