Controlled Wetting on Electrodeposited Oxide Thin Films: From Hydrophilic to Superhydrophobic

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ABSTRACT: We have explored how surface morphology and structure affect wetting properties of electrodeposited oxide thin films notwithstanding chemical modifications. Microstripes of self-assembled monolayers (SAMs) on gold were prepared using a microcontact printing (μCPI) technique, which served as molecular templates to guide the electrochemical deposition of zirconia in aqueous solution. The wetting properties of the thus-prepared zirconia oxide thin films are shown to be tunable; i.e., a wide range of wettability from hydrophilic to superhydrophobic can be obtained by simply varying the SAM template and the electrodeposition conditions (potential scan rate and number of cycles). In particular, a “two-tier” micro/nanoscale roughness was achieved on the gold substrate patterned with alternating stripes of 1-octadecanethiol and 6-mercapto-1-hexanol SAMs, which leads to a superhydrophobic surface (water contact angle $\sim$150°). Of great significance is the demonstrated ability herein to convert an intrinsically hydrophilic into a hydrophobic surface by changing the conditions for materials fabrication, which does not involve any chemical modifications.

1. INTRODUCTION

The wetting property of a solid surface is closely related to two factors, i.e., topographical structure (surface roughness) and chemical composition (surface energy).1,2 In nature, this is demonstrated by lotus leaves that have two roughness scales: micrometer bumps and nanometer hair-like features in addition to a wax layer to lower its surface energy.3,4 There has been mounting interest in the scientific community to explore a surface’s chemical and structural relationship to wetting properties. It is well-known that roughened surface structure increases water repellency considerably.5 The apparent contact angle on a uniform solid was described in Wenzel’s theory where the liquid is assumed to fill the grooves of the roughened surface.6 For a rough surface where the droplet sits on fractional areas consisting of the solid surface and air and does not fill the grooves, the modified Cassie’s equation should be used.5–7 Both models confirm the influence of topography on minimizing the surface energy and predict variations in contact angle as a function of surface roughness, suggesting the wettability may be tuned by changing its roughness.8 However, Wenzel’s equation predicts that enhancing the roughness will contribute to greater hydrophobicity only if the surface is initially hydrophobic. Therefore, according to this model a hydrophilic surface cannot be turned into a hydrophobic one by tuning its roughness, implying that it must be accompanied with a change in chemical composition of the surface. Thus, the conventional way of creating water-repellent surfaces has been to create rough structures on an already hydrophobic surface or to modify a rough surface with chemical functionalities that will lower the surface energy, such as fluorinated groups.9 In fact, Cassie noted over 50 years ago that surface structure can play an even more immense role in water repellency rather than any water-proofing agents.5 It is therefore of great interest to be able to create water repellency, without the use of water-proofing agents, by solely manipulating the surface structure. By and large, consideration of the role that surface topography vs chemical composition plays in controlling the wetting properties of a surface is of importance from both fundamental research and application perspectives.

Tuning a surface’s wetting properties by controlling the roughness and nanostructures has been the focus of many recent studies.3,4,7,10–13 Thus far, the creation of superhydrophobic surfaces in most cases has depended on chemical modification with alkyl or CF₃ groups subsequent to roughening the surface.1 Using inherently hydrophilic metal oxides to fabricate patterned surfaces was combined with subsequent chemical modifications, to obtain water-repellent films. For example, ZnO and TiO₂ surfaces that demonstrate reversible wetting between hydrophilicity and hydrophobicity by UV irradiation involve changes in surface composition.14–16 This method relies on the generation of electron–hole pairs that create surface defects more favorable to the adsorption of hydroxyl groups. Recent studies by Zhu and co-workers have shown that SnO₂ films could be made superhydrophobic by...
creating aligned nanorod morphology. In comparison to the hydrophilic property of “flat” SnO2 films, the nanorod surfaces have a low surface energy due to a composite surface of air and the film surface being formed upon in contact with water droplets, leading to the water-repellent behavior. Similarly, Wang et al. were able to create superhydrophobic tungsten droplets, leading to the water-repellent behavior. Similarly, pH to control the surface morphology. The demonstrated silicon master templates. Evaporated Metal Films Inc. (Ithaca, NY). Patterned 10 nm Cr followed by 100 nm Au) were purchased from 1). We chose zirconia as our model system because the preparation and characterization of these oxide thin films via electrochemical deposition have been well documented in the past. Herein we demonstrate that by varying the scan rate and number of cycles during the electrodeposition ZrO2 films can be fabricated to show a wide range of wetting properties, from hydrophilic to superhydrophobic.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. Octadecanethiol (98%), 6-mercapto-1-hexanol (97%), and ethanol (95%) were purchased from Aldrich (Milwaukee, WI) and used without further purification. Deionized water was obtained from a Barnstead EasyPure UV/UF compact water system (Dubuque, IA) with a resistivity of >18.3 MΩ-cm. Gold-coated glass slides were cleaned with “piranha” solution (3:1 mixture of concentrated H2SO4 and 30% H2O2) for 5 min at 90° to remove organic contaminants (CAUTION: use extreme care as piranha solution is explosive when in contact with organic materials). The substrates were patterned with the desired alkanethiolate self-assembled monolayers (SAMs) using the microcontact printing (μCP) technique. As shown in Figure 1(b), the PDMS stamp patterned with 20 μm stripes was “inked” with 1.0 mM solution of octadeclanethiol (C18) in 95% ethanol and dried under nitrogen. The gold surface was then stamped on for ~30 s. After being patterned with the −CH3 monolayer of the gold substrate (Figure 1c), the sample was placed in a solution of 6-mercapto-1-hexanol (C6OH, 1.0 mM, in 95% ethanol) for 30 min to have alternating stripes of CH3- and OH-terminated alkanethiolate SAMs (Figure 1d).

2.2. Electrochemical Deposition of Zirconia. In our electrochemical deposition experiments, the working electrode was a gold-coated glass slide; the counter electrode was a Pt wire; and the reference was a Ag|AgCl3 M NaCl electrode. Electrochemical deposition was conducted with an Autolab Electrochemical Analyzer (PGSTAT30, Eco Chemie BV, Netherlands) in a faraday cage. The gold working electrode was pressed against the bottom of a Teflon cell using an O-ring seal, exposing an area of 0.69 cm2. Zirconia films were formed from a solution of 5.0 mM ZrOCl2·8H2O and 0.1 M KCl in deionized water. Two different scan rates (40 and 20 mV/s) have been tested; the number of cycles was varied, but the potential scan range of +0.8 to −1.1 V was used unless noted otherwise. After deposition the films were dried under nitrogen gas; the films were then stored under ambient conditions for approximately one week to allow for complete and slow drying.

2.3. Surface Characterization. Wetting measurements on the prepared zirconia films were performed using a digital AST Optima contact angle apparatus with a horizontal light beam to illuminate the water droplet. Water droplet volumes of approximately 1.5–2.0 μL were delivered to the surface with micropipets (having an uncertainty of less than 10%) to measure the contact angles.

To analyze the surface morphology of the films, atomic force microscopy (AFM) images were obtained from a Topometrix Explorer AFM (8 μm-Z-Linearized scanner) using silicon nitride tips (Triangular D of MSCT-AUHW, Veeco Metrology group, resonance frequency 15 kHz, force constant 0.03 N/m). Images were acquired in contact mode and analyzed using Thermomicroscopes SPM Lab Software from which the root-mean-square (rms) roughness was calculated.

Scanning electron microscopy (SEM) images were obtained from either an FEI DualBeam Strata 235 or Nova Nano SEM 430. Electrochemically prepared ZrO2 films were imaged using secondary electron imaging (SEI) and grounded using carbon paste to avert charging of the sample. Typical accelerating voltage of 10 kV and magnification of ×5000 were used.

XPS spectra were acquired using a monochromatic X-ray source of Aluminum Ka (1486.7 eV) with an analysis area of 700 × 300 μm² with a step size of 0.05 eV and dwell time of 200 ms. The chamber pressure was maintained at 10−9 Torr during data acquisition. Hybrids of Gaussian and Lorentzian statistical models were used to model peak areas of high-resolution XPS (HR-XPS).

3. RESULTS AND DISCUSSION

3.1. Formation of the Molecular Templates. In this study, we are exploring the application of patterned SAMs as
molecular templates to control the electrochemical deposition of oxide thin films and to selectively alter their surface morphology (while maintaining the same chemical composition), with an ultimate goal of providing a better understanding of the relationship between surface microstructure and wetting properties. For this purpose, gold slides were patterned with stripes of CH₃-terminated SAMs using μCP (Figure 1c); the gold slides were also modified with alternating regions of CH₃- and OH-terminated SAMs (Figure 1d) by placing the CH₃ monolayer-patterned slides in a deposition solution of OH-terminated thiol.

In Figure 2(a), the SEM image of a gold substrate patterned with alternating “microstripes” of a C18 SAM and bare gold shows clear contrast. This is due to the difference in conductivity since the region patterned with the C18 monolayer is less conductive. When the substrate is patterned with alternating stripes of two different SAMs, the contrast is not as clear since the entire substrate is covered with organic molecules and has relatively similar conductivity. However, these surfaces can be imaged with AFM operated under lateral force mode (Figure 2b). The contrasting stripes of equal dimensions indicate the difference in the frictional force between the terminal groups (CH₃ vs OH) of the SAM and the AFM tip. Therefore, we confirmed that our gold substrates are indeed patterned with the respective monolayers according to the dimensions of the PDMS stamp (10 μm wide stripes).

3.2. Electrochemical Deposition of the Oxide Thin Films. Zirconia films were then prepared on the modified gold surface using electrochemical deposition in a dilute solution of ZrOCl₂ at different scan rates to examine if the monolayer template can guide the deposition of the zirconia film. Figure 3 shows the typical cyclic voltammograms (CVs) for the electrochemical deposition of ZrO₂ thin films onto differently modified Au substrates under varied experimental conditions (different scan rates and number of cycles). In contrast to the featureless anodic trace, two cathodic peaks at approximately −0.95 and −1.05 V were observed in all cases and indicate that the ZrO₂ deposition is an irreversible redox process. Both peaks are more pronounced for the initial scan in comparison with subsequent cycles; i.e., the peak currents gradually decrease, and the peak at −0.95 V eventually diminishes after 10 or 15 cycles.

It is widely accepted that electrochemical deposition of oxide thin films (e.g., ZrO₂) involves the generation of base (OH⁻) at the cathode surface (gold) by the following reaction:

\[
\text{ZrOCl}_2 + 2 \text{OH}^- \rightarrow \text{ZrO}_2 + \text{H}_2\text{O} + 2 \text{Cl}^-. \]

Figure 2. (a) SEM image of a gold substrate patterned with alternating “microstripes” of C18 SAM-covered and bare gold surface. The stripes of contrasting color indicate a difference in conductivity between the two regions. (b) Lateral force AFM image of the gold substrate patterned with the C18 and C6OH monolayer in stripes of equal spacing. The contrasting stripes indicate the different terminal groups (OH vs CH₃) in the C6OH and C18 region. A PDMS stamp with 10 μM stripes was used to prepare these samples.

Figure 3. CV responses of a gold electrode modified with patterned alkanethiolate SAMs under cathodic electrodeposition of a zirconia thin film (5 mM ZrOCl₂·8H₂O and 0.1 M KCl). (a) Au–C18: 10 scans at 40 mV/s. (b) Au–C18/C6OH: 10 scans at 40 mV/s. (c) Au–C18: 15 scans at 20 mV/s. (d) Au–C18/C6OH: 15 scans at 20 mV/s. The first and last scans showed a significant decrease in the peak current due to the film becoming increasingly resistant to the redox process.


\[ \text{ZrOCl}_2 \rightarrow \text{ZrO}^{2+} + 2\text{Cl}^- \]

\[ \text{ZrO}^{2+} + \text{H}_2\text{O} \rightarrow \text{Zr(OH)}_2^{2+} \]

\[ \text{Zr(OH)}_2^{2+} + 2\text{OH}^- \rightarrow \text{Zr(OH)}_4^{-} \]

\[ \text{Zr(OH)}_4^{-} \rightarrow \text{ZrO}_2 + 2\text{H}_2\text{O} \]

The detailed mechanism for the electrochemical formation of zirconia may still deserve further understanding: it is evident that the CV responses shown in Figure 3 are dependent on the molecular template on the gold electrode, the scan rate, and the number of cycles. At the same scan rate, the peak currents for C18-modified gold electrodes (Figure 3a/3c) are clearly higher than those from the C18/C6OH modified cases (Figure 3b/3d). This result indicates that the SAMs act as a resist to block the electrochemical deposition, allowing deposition to occur on the bare gold regions (Figure 1c) where base can be cathodically generated to form ZrO₂. By patterning the SAMs on the surface, it becomes feasible to control the growth of the zirconia film to selective areas, although this would be rather complex when the surface is modified with alternative C18/C6OH stripes (Figure 1d). Nonetheless, the CVs shown in Figure 3(b) and (d) are indicative that substantial accumulation of ZrO₂ also occurred on the surfaces fully covered with SAMs.

To further confirm the zirconia films were deposited on the surface of SAM-modified Au, these films were first characterized by X-ray photoelectron spectroscopy (XPS). Figure 4(a) shows the XPS elemental survey scans of the films formed on both Au–C18 and Au–C18/C6OH under different scan conditions. The peaks corresponding to O, Zr, and C elements are clearly observed in all cases. The two deconvoluted peaks shown in Figure 4(b) are characteristic of fully oxidized zirconium in the 4+ state and represent a splitting into two spin orbital components 3d_{5/2} and 3d_{3/2}. The binding energies of these two peaks are 182.9 and 185.5 eV, respectively, which are in good agreement with the literature values.

Despite the different modifications, the peak of Au 4f was clearly identified in the cases of slow scan rate (20 mV/s; spectra i and ii); this peak is rather weak (iv) or not discernible (iii) in the case that a faster scan rate (40 mV/s) was employed. As the gold is the substrate material that is covered with the organic monolayer and the oxide films, the above differences indicate that the thus-formed ZrO₂ films may have very different thicknesses and/or porosities.

Zirconia thin films formed from low-temperature deposition methods are typically amorphous, having a cracked mud appearance due to the nonuniform contraction of the wet coating on drying. To investigate the thickness and structure of the electrochemically deposited ZrO₂ films on the modified Au substrates, SEM was first employed to examine the cross section of the films. Figure 5 shows that the thickness of the films varies significantly upon changing the scan rate and number of cycles: at a scan rate of 40 mV/s (10 cycles), the ZrO₂ films are below 200 nm (137 nm for Au–C18 and 166 nm for Au–C18/C6OH as shown in Figure 5a and 5b, respectively). At a slower scan rate (20 mV/s; 15 cycles), the film grew as thick as 800–900 nm for both C18 and C18/C6OH SAM-modified gold electrodes. More importantly, the SEM images show that all the films are not compact; i.e., vacancies or pores can be clearly identified in the films. Particularly for the films prepared under slow scan rate (20 mV/s: Figure 5c and 5d), there are cracks (pores) all the way through to the electrode surfaces. The size of these pores is in
the range of hundreds of nanometers for the films prepared on Au–C18 and smaller on the surface modified with C18/C6OH SAMs. The existence of these pores is likely accounting for the observed Au 4f peaks in Figure 4(a); in contrast, the thinner films prepared under fast scan rate (40 mV/s: Figure 5a, 5b) are more uniform (lack of pores or cracks).

Atomic force microscopy (AFM) was used to further examine the topography of the zirconia films. At a relatively fast scan rate (40 mV/s) there is pronounced confinement (height difference) of the film to regions of bare gold (Figure 6a); in contrast, the thinner films examined by the electrochemical parameters alters the wetting properties of the surface.

Figure 6. AFM imaging of zirconia films patterned on monolayer templated gold substrates. Inset: Contact angle measurements for each film. (a) C18 patterned lines: 10 scans at 40 mV/s, 115°. (b) C18–C6OH patterned lines: 10 scans at 40 mV/s, 100°. (c) C18 patterned lines: 15 scans at 20 mV/s, 40°. (d) C18–C6OH patterned lines: 15 scans at 20 mV/s, 145°. The underlying surface morphology dictated by the chemical heterogeneity of the surface)

also occurred due to defects within the monolayer; nevertheless, deposition is highly favored along the bare Au regions. This is consistent with the observation of O’Brien et al. in their studies using C18 SAMs as molecular resists for “localized” electrodeposition of cobalt. Similarly, Zhou et al. used patterned SAMs prepared by μCP as templates to direct the deposition of polypyrrole microstructures on gold and silicon.

For the CH3/OH systems, rather surprising results were observed (Figure 6b). In this case, the entire gold substrate is covered with a passivating monolayer of C18/C6OH in alternating stripes; therefore, cathodic generation of base is significantly hindered across the entire surface. However, there are limited regions where the cathode surface is not totally blocked by the monolayer such as at defects or pinholes in the monolayer. In fact, we observed that at high scan rates (>40 mV/s) a different pattern is observed in comparison to the C18–bare gold system. The C18/C6OH system displays a greater periodicity of confinement than the C18/bare gold system having similar “mountain/valley” features (compare Figure 6a with 6b). This is seen in the AFM image of Figure 6b, where zirconia is confined to ~5 μm stripes having a height of about 170 nm (Figure 5b). This type of confinement was only observed using two thiol molecules of both different functional groups and different alkyl chain lengths, such as in our C18/C6OH system. There are a few possibilities that lead to these results such as deposition may be more favorable at interfaces of the mixed SAMs. Differences in applied pressure to the stamps during μCP may also contribute to the differences. Also, when the substrate patterned with C18 is placed in the C6OH deposition solution, spreading and diffusion of the methyl-terminated SAMs may alter the pattern of the molecules on the surface, which in turn would affect the subsequent deposition confinement. However, these investigations are beyond the scope of this work, which focuses primarily on the relationship between surface structure and wetting.

3.3. Correlation between Film Morphology and Wetting Properties. Varying the electrochemical parameters resulted in the formation of distinct film morphologies that demonstrate different wetting properties. The contact angle measurement on the C18–bare gold surface deposited with zirconia was found to be 115 ± 3° (Figure 6a) for 10 scans at 40 mV/s. For gold substrates patterned with C18/C6OH, under similar deposition conditions, a contact angle of 110 ± 2° is observed (Figure 6b), slightly lower than the C18/bare gold system.

The molecular template for both these systems helps to tune the surface morphology and significantly increase the hydrophobicity of the film. In comparison, a bare gold substrate (not modified with a molecular template) when deposited with a zirconia film is very hydrophilic with a contact angle <40°. Zirconia films are inherently hydrophilic due to the surface being hydroxyl terminated; i.e., the surfaces of ZrO2 are primarily “covered” –OH groups. This has been confirmed by FT-IR analysis along with deuterium exchange studies with strong absorption bands in the –OH region. Therefore, the above results are remarkable since a hydroxyl-terminated surface has been made hydrophobic (without any changes in the chemical heterogeneity of the surface) via manipulation of the surface morphology. It should be noted that the zirconia films need to be left to dry under ambient conditions for approximately one week prior to wetting studies. During the formation of these films in aqueous media, water can enter the spaces between the nanostructures and be trapped. This was observed when the contact angle of these films was measured immediately after deposition and drying under N2, where the films were found to be initially hydrophilic and at times water droplets completely wet the surface. We believe the slow drying process allows for the enhanced roughening/texturing of the surface, leading to the subsequent hydrophobic behavior. Thereafter, these films sustained their hydrophobic property after being wetted numerous times for contact angle measurements.

At the slower scan rate of 20 mV/s, there is a significant loss of film confinement (in terms of height difference) on the gold substrates patterned with stripes of C18 SAMs. We believe at these slow scan rates there is more time for diffusion-controlled processes to occur. For systems patterned with alternating stripes of –CH3-terminated SAMs, 20 mV/s results in the deposition of larger particles (Figure 6c). Therefore, no confinement and the “mountain/valley” features are no longer visible, which results in a decrease in the surface roughness. To create thicker films a scan range of +0.8 to −1.2 V was used in this case. Water droplets placed on these systems wet the surface and have contact angles of around 40°.

Interestingly, when the substrate was patterned with both CH3- and OH-terminated SAMs in alternating stripes (the C18/C6OH system) and scanned at 20 m/V/s for 15 scans the film was found to drastically improve its hydrophobicity into the superhydrophobic region with a contact angle of ~150°.

Figure 5. Atomic force microscopy images of silicon samples patterned with stripes of C18 and C6OH SAMs. (a) 20 μm C18 patterned lines: 5 scans at 20 mV/s. (b) 20 μm C18 patterned lines: 15 scans at 20 mV/s; a rougher surface is observed. The underlying surface morphology is dictated by the chemical heterogeneity of the surface.
Due to the slower scan rates, there is a loss of height difference; nevertheless, the underlying template still acts to affect the resulting film morphology. Two different features are clearly visible with these films, with the interface between the two SAMs having larger “cracks”. The AFM image in Figure 6d shows two distinct morphologies on the microscopic scale in the film; on the finer scale the nanometer “bumps” on the surface are reminiscent of the “nanometer hairlike” features of the lotus leaf. This morphology also is reminiscent of the larger-scale roughness on the lotus leaf that has epidermal cells in the micrometer scale. We believe that the coexistence of these roughness scales plays a significant role in enhancing the hydrophobicity of the inherently hydrophilic zirconia film. The vast increase in contact angle was achieved simply by increasing the roughness of the surface without any further chemical modification of the film.

This observation of making an inherently hydrophilic material into a hydrophobic one cannot be described by Wenzel’s equation

\[ \cos \theta' = r \cos \theta \]  

(1)

where \( \theta' \) is the apparent water contact angle; \( r \) is the ratio of the true wetted area to the apparent area (which is essentially the surface roughness factor); and \( \theta \) is the contact angle exhibited by a flat surface of the same chemical nature. According to this equation, there are limitations for a wetted hydrophilic surface to become hydrophobic by simply changing the roughness factor \( r \). Therefore, for the roughened hydrophobic surfaces, they must follow Cassie’s law for a composite surface (trapped air bubbles and oxide films)\(^5\)

\[ \cos \theta' = -1 + f(1 + \cos \theta) \]  

(2)

where \( \theta' \) and \( \theta \) are the same as in eq 1 and \( f \) is the fraction of solid oxide in contact with water. In this case, the droplet sits on fractions of air and solid and does not intrude into the bumps on the surface. Therefore, although the surface of the film is terminated with hydrophilic (OH) groups, the chemical nature of the film does not seem to play a dominant role in dictating the wetting properties in this case. Rather, the nanometer roughness of the film, which has the ability to support the droplet on a composite surface of air and substrate, contributes significantly to the ultrahydrophobic behavior. Extrand has recently examined varied experimental parameters for creating water-repellent surfaces.\(^1\) He also noted that in most cases a liquid deposited on a rough surface will spread and engulf surface asperities; however, when the drop is suspended on top of surface asperities and air pockets, this gives rise to extremely large contact angles of 140–180° characteristic of a superhydrophobic or super-repellent surface. It was demonstrated that three conditions must be met for a surface to demonstrate water-repellent behavior: (1) the interaction of the liquid with the surface features must direct forces at the contact line upward, (2) the surface forces must be large enough to support the liquid against the downward pull of gravity, and (3) the surface features must be tall enough that liquid protruding does not contact the underlying solid.\(^1\) We believe that these criteria are met in our film of the C18/C6OH systems, which demonstrates water-repellent behavior with a contact angle in the range of 140–160°.

To study the dependence of the contact angle on the number of scans and scan rates (which eventually changes the thickness and roughness of the thus-formed thin films), two systems were studied (Figure 7). Gold substrates were modified with C18 patterned in 20 \( \mu \)m stripes, and zirconia was deposited at either 20 or 40 mV/s while the number of scans was varied. For the systems scanned at a rate of 20 mV/s, the scan range was from +0.8 to \(-1.2 \) V, which allowed for thicker films to form on the surface, whereas the systems scanned at a rate of 40 mV/s were scanned in a range of +0.8 to \(-1.1 \) V, allowing for formation of thinner films. It is evident in Figure 7 that there is a clear effect of the electrochemical parameters on the water contact angles. At 40 mV/s as the number of cycles increased from 5 to 10, the contact angle increases. Under these conditions the zirconia film could be tuned from 95° (for 5 cycles) to a hydrophobic 121° (for 10 cycles). The reason for this increase is that the surface is continually becoming rougher, so that the droplet may sit on regions of air and the film (Cassie’s model as noted above).

The increase in roughness was monitored with AFM where the root-mean-square roughness \((f_{\text{RMS}})\) was calculated based on eq \(^3\)

\[ f_{\text{RMS}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (z_i - \xi)^2} \]  

(3)

where \( z_i \) is the apparent water contact angle; \( r \) is the ratio of the true wetted area to the apparent area (which is essentially the surface roughness factor); and \( \theta \) is the contact angle exhibited by a flat surface of the same chemical nature. According to this equation, there are limitations for a wetted hydrophilic surface to become hydrophobic by simply changing the roughness factor \( r \). Therefore, for the roughened hydrophobic surfaces, they must follow Cassie’s law for a composite surface (trapped air bubbles and oxide films)\(^5\)

\[ \cos \theta' = -1 + f(1 + \cos \theta) \]  

(2)
formed were very hydrophilic, having contact angles of approximately 30° or less. As more scans were conducted, the films became more and more hydrophilic. This trend is opposite to the films formed using the molecular templates, where as more scans were run the film would increase its hydrophobicity. As a result, it is clear that the molecular templates play a key role in guiding the deposition of these zirconia films to create surfaces with roughened features; having these special surface features is necessary for creating films with increasing hydrophobicity.

Tuning the wetting properties of a surface involves many factors such as modifying the chemical heterogeneity and/or surface roughness. We have demonstrated that it is possible by simply altering the surface roughness of an inherently hydrophilic zirconia film to make such a hydrophilic material hydrophobic without any further chemical modification. This was accomplished by the use of μCP to create molecular templates on the surface to guide the deposition of zirconia allowing for the film to be confined and the surface morphology to be controlled microscopically. By simply altering the structure of the surface, we believe it is possible to create surfaces with an even greater water-repellent behavior; however, this would involve greater control of surface patterning for which further studies are warranted.

4. CONCLUSION

We have shown that superhydrophobicity can be achieved simply by an increase in the nanometer-scale surface roughness of an inherently hydrophilic film. By varying the roughness through electrochemical deposition it is possible to make such films water repellent without further chemical modification. Although the lotus leaf and other water-repellent materials are known to owe their behavior to both surface roughness (bumpy epidermal cells of the plants) and chemical nature (waxy cuticles), there is much to be learned from exclusively modifying the surface by varying just one of these parameters to establish certain limits such as the roughness scales needed for superhydrophobicity. The present work is an example of our continued efforts to understand such trends and principles in terms of surface roughness and chemical heterogeneity with the aid of molecular templates. Furthermore, of great interest would be deeper studies into the dynamic wetting properties of these surfaces such as we have done for gold surfaces modified with SAMs.\(^37\)\(^38\) This would involve monitoring the evaporation profiles and comparing whether there is any correlation between their direct wetting hysteresis and evaporation hysteresis for these hydrophobic and even superhydrophobic oxide thin film surfaces.

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Notes

The authors declare no competing financial interest.

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