Solution-Deposited Amorphous Titanium Dioxide on Silicone Rubber: A Conformal, Crack-Free Antibacterial Coating

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Controlled formation of thin oxide films on polymers provides an increasingly important tool for modifying the polymer interface without changing its bulk properties. The successful application of a titania thin film by liquid phase deposition (LPD) from water under near-ambient conditions onto polydimethylsiloxane (PDMS) substrates has been achieved. This offers a convenient, non-line-of-sight-limited method for imparting titania-like properties to the surface of the PDMS elastomer. Conditions have been found for priming the surface of the PDMS to provide for good adhesion of the oxide layer and a suitable combination of film deposition and film drying conditions are described that provide a conformal crack-free titania coating on the PDMS. This is the first report of LPD oxide formation on an elastomer. The application of such titania coatings to controlling bacterial adhesion and growth on the polymer surface is also described. The adhesion of both Gram-negative and Gram-positive bacteria to the modified surfaces is reduced. This reduction is further enhanced by UV irradiation of the TiO_2 overlayer prior to introduction of the bacteria.

Introduction

Microbial adhesion to surfaces and the formation of a biofilm at the interface between a man-made biomaterial and the biological environment are often responsible for sustained inflammatory processes and for the ultimate failure of biomedical devices such as vascular and urinary catheters, vascular implants, heart valves, and prostheses. In recent years, considerable research effort has been focused on creating antibacterial coatings on the surfaces of materials ranging from garments to implantable medical devices.[1,2]

Silicone rubber is one of the most widely used elastomers in rehabilitation devices and biomedical implants because it has excellent mechanical properties and relatively good biocompatibility. However, it is prone to biofouling, and this can be a major cause of patient discomfort and even clinical failure in many applications. Numerous antibacterial treatments have been applied to silicone rubber,[3–18] but none have proven completely effective.

The ability of TiO_2 coatings to influence bacterial adhesion has been demonstrated.[19] There is also extensive experimental support for the biocidal action of TiO_2, particularly for photocatalytic disinfection.[19,20] Different types of TiO_2-coated materials possess deodorizing, antibacterial, and self-cleaning properties under low-intensity UV light.[21,22] However, it has to date been difficult to make such oxide coatings on the surface of silicone rubber substrates because of problems with the adhesion between the oxide coating and the rubber substrate.[23–25] Moreover, line-of-sight limitations

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prevent application of many coating methodologies to the complex topography of silicone rubber-coated medical devices.

Various research groups,[26–32] our group among them,[33–35] have reported the creation of oxide films on polymers by deposition from aqueous solution under near-ambient conditions. Successful extension of this work to elastomers like silicone rubber would provide an important tool for the surface modification of this important class of materials. Among other applications, it would offer the potential for limiting bacterial adhesion and biofilm formation on silicone rubber-coated implants. This is a particular challenge in light of the combination of hard and soft material that would arise by attaching an oxide to an elastomer.

We report herein the liquid phase deposition (LPD) of amorphous TiO_2 thin films on the surface of polydimethylsiloxane (PDMS). The coating is achieved under near-ambient conditions and, by depositing a sufficiently thin oxide layer and using a controlled humidity drying protocol, crack-free conformal surface films can be achieved. As a measure of the degree to which this surface modification can be useful, the extent to which these coatings control bacterial adhesion was also examined. Challenging the titania-coated PDMS with various kinds of bacteria has provided an overview of the effectiveness of such coatings in limiting the attachment and growth of a spectrum of bacteria on oxide-coated surfaces.

Material and Methods

Titania−PDMS Surface. Experiments were performed on PDMS sheets supplied by Degania Silicone Ltd. (thickness 0.5 mm). The as-received sheets were cut into disks (diameter 15 mm) which were washed with ultrapure water (resistivity 18 MΩ·cm) and ethanol and dried under nitrogen. Prior to titania coating, the surface of the PDMS was pretreated by one of two methods: (I) samples were exposed to an air plasma (Harrick, model PDC-3XG) at a pressure of 0.3 mmHg and 18 W power for 5 min or (II) samples were dipped into a solution of 20% H_2SO_4 in water for 15 min. Samples cleaned and activated by method I were completely wetted by water (e.g., $\theta^{H_2O}_{adv} < 10°$), indicating the hydroxylated (Si−OH) nature of the substrate surface. Acid conditions (method II) do not dramatically change the wetting properties of the surface ($\theta^{H_2O}_{adv} \sim 115°$).

The freshly activated PDMS samples were placed in the titania deposition solution (0.3 M H_3BO_3 and 0.1 M $(NH_2)_2TiF_6$ in water, pH = 3.88, at room temperature).[36] The titania layers examined in this work were formed either by direct deposition for 8 h from such a freshly prepared solution or by a 4 h deposition from such a solution that was first aged for 18 h and then filtered through a 0.45 μm, 7 bar max filter (Schleicher & Schuele). The aged/filtered solution gave thinner coatings. The TiO_2-coated PDMS was rinsed in methanol before drying by controlled humidity, as described earlier.[33] Adhesion of the oxide films was qualitatively assessed on the basis of the ability to withstand a simple tape test and by examining the film for cracks/delamination after 30 min sonication in water in a bath sonicator (Telsonic model TPC-15; 75 W).

Surface Characterization. The surface morphology of the samples was assessed by scanning electron microscopy (SEM JEOL 840). To determine the thickness of the titania coating, a cross-sectional sample was prepared using a focused ion beam system (FIB Strata 400SS dual-beam) with characterization by STEM.

Rinsing in methanol and controlled humidity drying at 70° provided crack-free amorphous TiO_2 films when using the filtered, slower growing deposition solution.[33,34] The thicker films provided by deposition from a freshly prepared titania deposition solution show micron-sized cracks. Optical microscopy was used to estimate the degree of film cracking. Such analyses were always done on four separate areas on each coated sample and were quantified using "ImageJ" image analysis software (freeware). The crack percentage was calculated from the ratio of white to black pixels. The data window gives an area of about 1244 × 1296 pixels.

The water contact angles of PDMS that had been exposed to air plasma or to aqueous acid or that had been coated with TiO_2 were measured using a contact angle goniometer (Rame-Hart model 100). About 1 μL of deionized water was placed on the surface. The reported contact angles are the average of five measurements, each done at a different point on the surface.

Atomic force microscopy (AFM) measurements were carried out with the Nano-Scope Dimension 3100 controller. Tapping-mode scans were performed with Al-coated silicon cantilevers/tips (Digital Instruments) at ambient conditions using a 100 μm^2 $x-y$ range scanner. The root-mean-square roughness (R_q) was calculated from 2 × 2 μm^2 sized height images. Since the roughness parameter is line-dependent and all height values are relative, no flattening and plane-fitting procedures were used. The surface roughness was measured at a minimum of three different points on each sample.

XPS spectra were done on a Perkin-Elmer ESCA 5400 using a Al Kα source at a base vacuum of 10^{-9} Torr. The angle between the X-ray beam and sample was 90°. High-resolution multiplex spectra were collected on a ~2 × 3 mm spot, using 40 eV pass energy and a resolution of 50 eV. The spectrometer was calibrated according to standard procedures using Au $4f_{7/2}$ and Cr $2p_{3/2}$ peaks at 83.98 and 932.67 eV, respectively. Survey spectra were collected from 98 to 110 eV with a pass energy of 20 eV. The binding energies were referenced to the C 1s binding energy of the hydrocarbon of the PDMS at 285 eV.

Bacterial Adhesion. The bioadhesion tests were all done on samples that had been pretreated by the air plasma method and that had the thinner titania coatings (from aged-filtered solutions). Five strains of bacteria were used in these experiments: *Escherichia coli* (1313, obtained from Sheba Medical Center of Tel Hashomer), *Pseudomonas aeruginosa* (1316), *Staphylococcus aureus* (ATCC 25923), *Acinetobacter baumannii* (obtained from Meir hospital, Kfar Saba), and *Staphylococcus epidermidis.*

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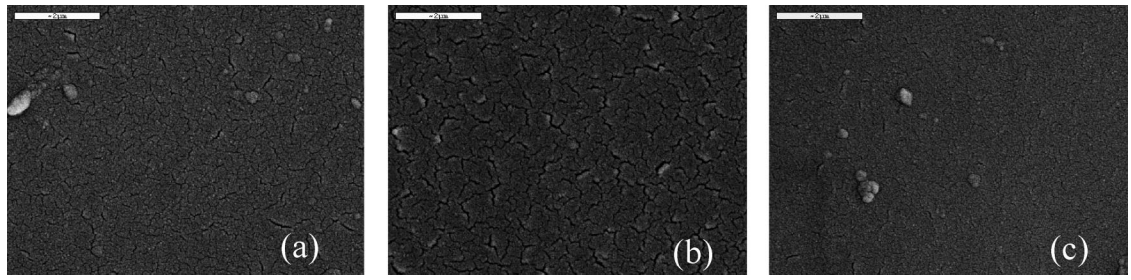

Figure 1. SEM images of (a) as-received PDMS, (b) PDMS after 5 min exposure to air plasma, and (c) PDMS after 15 min immersion in 20% H_2SO_4.

Each bacterial strain was transferred from a pure stock culture and was streaked individually onto agar plates, grown at 37 °C for 24 h, and then resuspended in nutrient broth medium at a cell concentration of 0.15 optical density. In order to evaluate the adhesion of bacteria to variously treated PDMS surfaces, the bacterial suspension was transferred to a 24-well plate presenting silicone rubber, with or without a TiO_2 coating. The position of the coupons in the plate did not affect the experiments. The samples were incubated at 30 °C for 24 h. After incubation, bacteria were washed from the surfaces of the coated silicone rubber with saline solution (five times). For SEM evaluation, fixator (Karnovsky solution) was added to each well.

Titania has well established photoredox-based bacteria-killing ability such that there was no need to examine this issue.[19,20,37–39] We were, however, interested in the possible application of UV irradiation as a tool for pretreating surfaces. Thus, we did include in this study samples of both coated and uncoated PDMS that had been pretreated with UV radiation.

Bioadhesion tests were conducted on samples of untreated PDMS and on PDMS that had been variously cleaned and coated with TiO_2. Some of the samples of PDMS with and without TiO_2 coating were fully exposed to UV light (Lamp manufactured by Vilber Lourmat, model VL-6LC, 6 W at 254 nm) for 1 h before growing the bacteria. Samples that were exposed to UV light were removed from the UV light chamber immediately before treatment with the solution of bacteria. The nominal wavelength of the UV light was 254 nm, and a consistent distance of 5 cm was maintained between the sample and the lamp during the UV exposure.

Visualization of the Bacteria on the Surface of Variously Treated PDMS. The bacteria were cultured as described above. After the indicated times, fixation of samples was performed according to a modification of the triple fixation GTGO method for SEM. Briefly, the samples were fixed with 2.5%/2% glutaraldehyde/paraformaldehyde in phosphate buffer (PBS), pH 7.2 (Karnovsky solution), followed by poststaining in 2% OsO_4. The third fixative was 2% tannic acid−guanidine hydrochloride. After fixation, the cells were dehydrated in graded ethanol solutions, and then the ethanol was exchanged for Freon 113-tf, again using graded solutions. After that, the samples were air-dried and gold-coated with 10 nm Au in a sputter coater and examined using a JEOL 840 scanning electron microscope (SCI detection mode). The microscope was operated at accelerating voltages of 25 kV, with a high emission current of 1×10^{-10} A and a working distance of 15 mm.

Results and Discussion

The initial cleaning and/or priming of the PDMS involved exposure to an air plasma or to a solution of 20% H_2SO_4. The freshly cleaned PDMS was used as a substrate for TiO_2 deposition. Treatment with either air plasma or aqueous acid was necessary to achieve good adhesion of titania to the PDMS surface. Without such treatments, the titania adheres very poorly to the PDMS surface. SEM analysis (Figure 1) shows that if the air plasma treatment is limited to 5 min and the aqueous acid treatment is limited to 15 min, there is no significant erosion of the PDMS surface.

After air-plasma exposure, the water contact angle of the PDMS decreases from 115° to 10°. This result is consistent with earlier reports that suggest a plasma-induced surface oxygenation of PDMS with increased hydrophilicity and improved bonding of PDMS to other surfaces.[40,41] XPS analysis showed the atomic composition of the surface of the as-received PDMS to be 35% Si, 23% O, and 42% C. When exposed to air plasma, the carbon content decreased (28%), whereas the oxygen content increased (39%) and the silicon content remained between 33 and 35%—consistent with substantial surface oxidation. High-resolution analysis of the Si 2p XPS signals observed before and after air-plasma exposure showed peak broadening and a shift toward higher binding energies at ∼103.7 eV (e.g., Figure 2). This is consistent with the formation of a silica-like (SiO_x) surface.[42–44]

By way of contrast, etching the PDMS in dilute aqueous H_2SO_4 (20%) did not significantly change its wetting properties or the shape of the silicon signal in the XPS (compare parts A and B of Figure 2) or its surface atomic composition (37% Si, 26% O, and 37% C). These results highlight the difference between the two priming procedures. Exposure to air plasma introduces new silanol (Si−OH) groups on a silica-like layer while oxidatively removing some of the surface alkyl groups (e.g., $Si-CH_3$). Immersion in dilute H_2SO_4 cleans the surface with, perhaps, a minimal amount of Si−O−Si hydrolysis.

Both the air plasma and acid-pretreated PDMS samples could be coated uniformly with TiO_2 by liquid phase deposition (LPD). Deposition from water (0.3 M H_3BO_3, 0.1 M $(NH_4)_2TiF_6$, pH 3.88) at room temperature gave amorphous titania films[45] that adhered well to the air plasma or H_2SO_4-treated PDMS surfaces. Figure 3 shows the resulting

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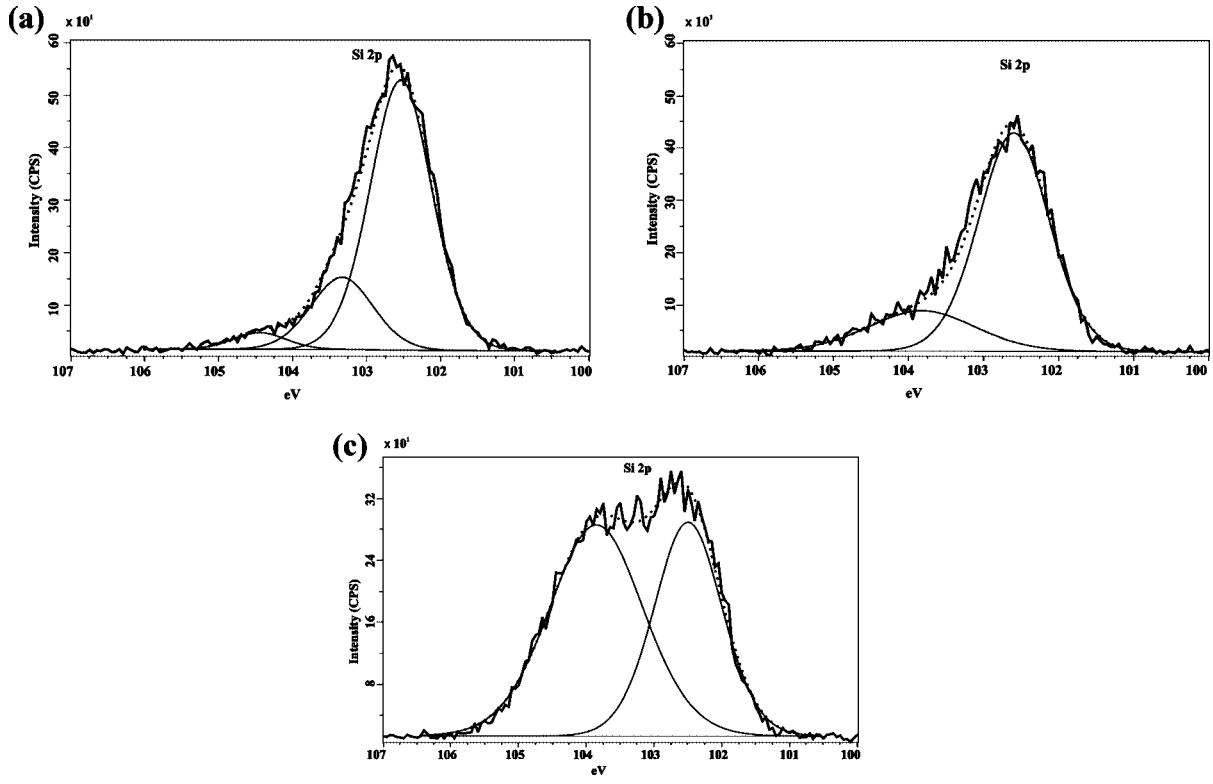


Figure 2. Silicon XPS spectra (including curve fitting) of (a) as-received PDMS, (b) after treatment with 20% H_2SO_4, and (c) after treatment by air plasma. The peak at 102.5 eV is that expected for the silicon in PDMS, while the peak at ~103.7 eV corresponds to SiO_x.

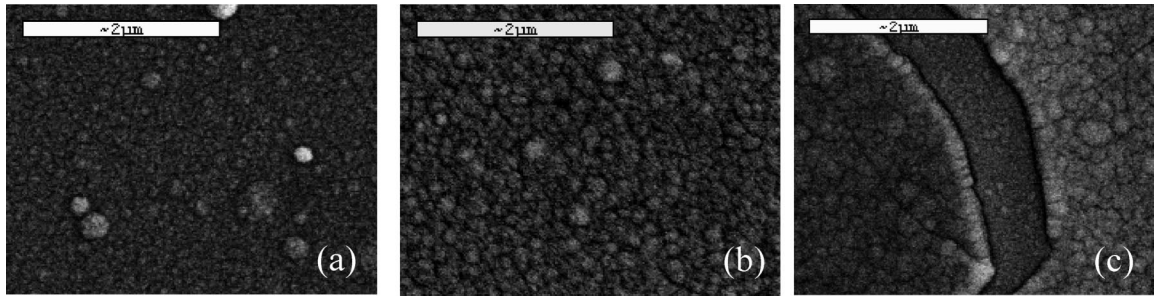


Figure 3. SEM image of the surface of PDMS with TiO_2 layer deposited from a freshly prepared aqueous deposition solution after (a) air plasma pretreatment or after (b) etching in 20% H_2SO_4. (c) Representative crack from a titania coating on an acid-pretreated surface.

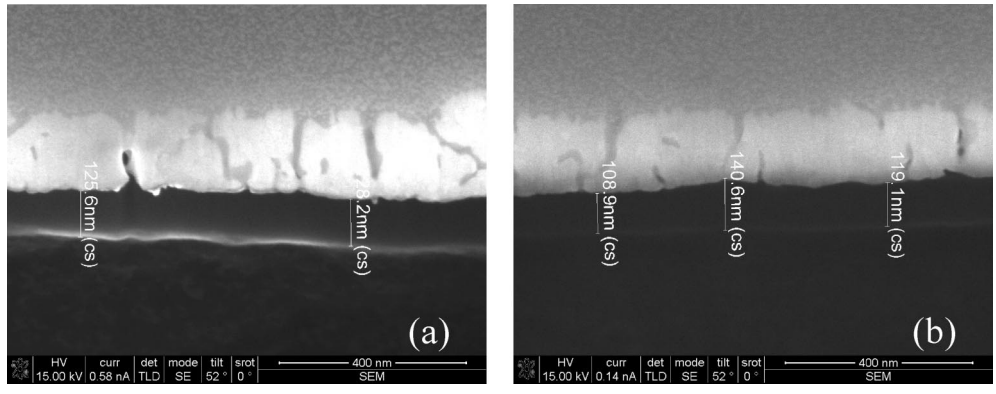


Figure 4. Cross-sectional view of PDMS coated with TiO_2 after treatment by (a) air plasma or (b) dipping in 20% H_2SO_4. The black lower level is PDMS, second layer is TiO_2, the thick irregular white layer is Au coating, and the gray top level is Pd. Both the Au and the Pd are part of the microscopy process.

TiO_2-coated surfaces. The thickness (Figure 4) of the TiO_2 layer (8 h deposition from a freshly prepared solution) was ~135 nm whether the PDMS was pretreated with air plasma (125–128 nm) or with H_2SO_4 (109–141 nm).

As is evident in comparing the images in Figure 3, coatings using the freshly prepared LPD solution gave surfaces with some areas that were uniform and crack-free but also with significant cracks. Despite extensive efforts to use controlled

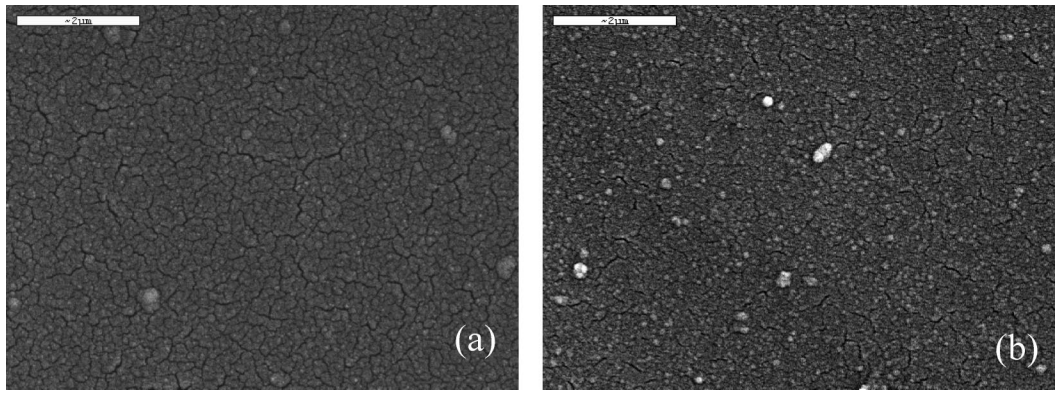


Figure 5. SEM image of the surface of PDMS coated with titania using a filtered deposition solution after pretreatment with (a) air plasma or (b) 20% H_2SO_4.

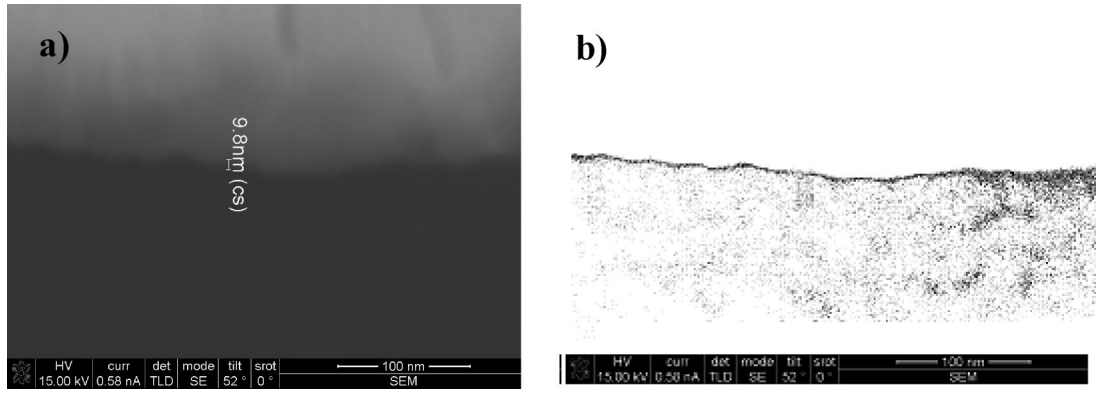


Figure 6. (a) Cross-sectional view of PDMS after air-plasma pretreatment, coated with prefiltered TiO_2 deposition solution. The lower section is PDMS, middle layer is TiO_2, and the top layer is the Au coating. (b) ImageJ analysis software image titania thin film on PDMS coated with prefiltered TiO_2 deposition solution.

humidity drying to eliminate these cracks, no drying procedure could be found to completely solve the problem for TiO_2 films of this thickness on PDMS. The percentage of the surface area represented by the cracks (as determined by ImageJ analysis software) ranged from 2.7 ± 0.8% for the samples that had been primed by air plasma to 7.9 ± 2.5% for samples primed by the acid etch.

By filtering the titania deposition solution, we remove its turbidity and do not allow this initially formed oxide to contribute to film growth. The aged solution has a slower rate of TiO_2 nucleation, and thus the resulting titania surface films will form more slowly and will be thinner for comparable periods of film growth. They will also be comprised of smaller grains. Figure 5 shows the surface of PDMS after coating by a filtered TiO_2 deposition solution. In contrast to the thicker layer deposited from freshly prepared LPD solutions (Figure 3), in this case, the surface topography of the titania coating is smooth and crack-free. These films are estimated to be ∼10 nm thick. Cross-sectional SEM would have shown a clear layer had it been thicker than 20 nm. However, as shown in Figure 6a, the film is poorly defined, and we assume it to be ∼10 nm. We support this estimate by an image processed picture (ImageJ software) as shown in Figure 6b. This very thin film of titania is sufficiently uniform and crack-free (while still being completely adherent) so that it is suitable for practical use. All measurements of film properties and bacterial adhesion reported below were on such thin films.

The stability of the titania coatings was assessed by a combination of tape tests and sonication. All of the TiO_2-on-PDMS coatings reported herein were found to be stable to 30 min of bath sonication in water and were sufficiently adherent so that they could not be removed by a standard tape test.

Tapping mode AFM analyses provided further insight into the topography and texture of the variously treated PDMS samples. Figure 7 shows the AFM images of the as-received PDMS as well as after air plasma and after the acid etch. It is interesting to note the relatively smooth surface of the as-received PDMS (R_q = 3.1 ± 0.4 nm) as compared to the modest increase in roughness in the air plasma-treated surface (R_q = 5.9 ± 0.6 nm) and the significant roughening of the acid-etched surface (R_q = 9 ± 0.3 nm). The increased roughness of the PDMS after air-plasma treatment may be caused by the formation and collapse of the silica-like layer[42] suggested by the XPS results (above). The surface texture of PDMS after immersion in dilute acid is likely the result of partial degradation of the PDMS.

AFM was also used to study the TiO_2 surfaces (Figure 8). In general, the roughness of the TiO_2 film is less than that of the pretreated PDMS substrate. That is, the air plasma-treated PDMS had a roughness of R_q = 5.9 ± 0.6 nm, and after application of the thinner titania film (from the filtered solution) it became somewhat smoother (R_q value of 3.9 ± 0.3 nm). Similarly, the acid-treated surface was relatively rough (R_q = 9 ± 0.3 nm), and after deposition of the thinner titania layer it is smoother (R_q = 6.3 ± 0.4 nm). We thus

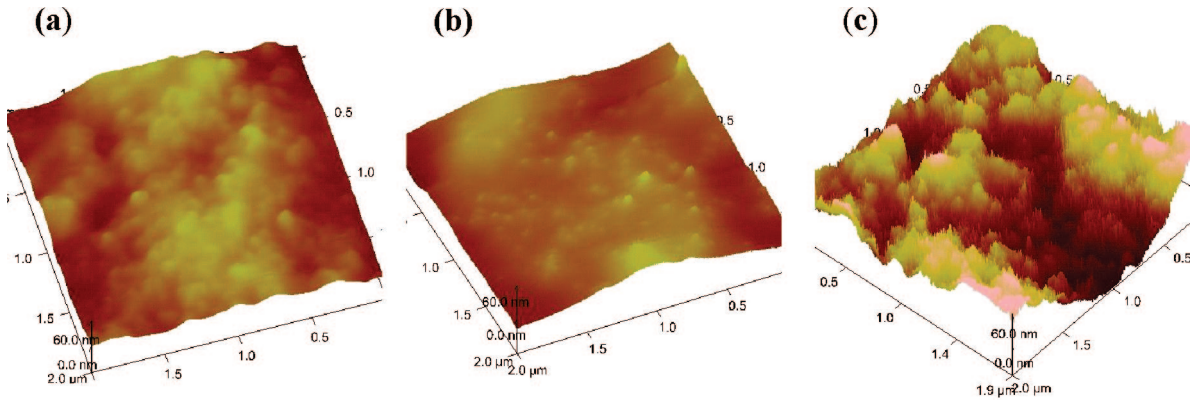


Figure 7. AFM images of (a) as-received PDMS, (b) air plasma-treated PDMS, and (c) H_2SO_4-etched PDMS.

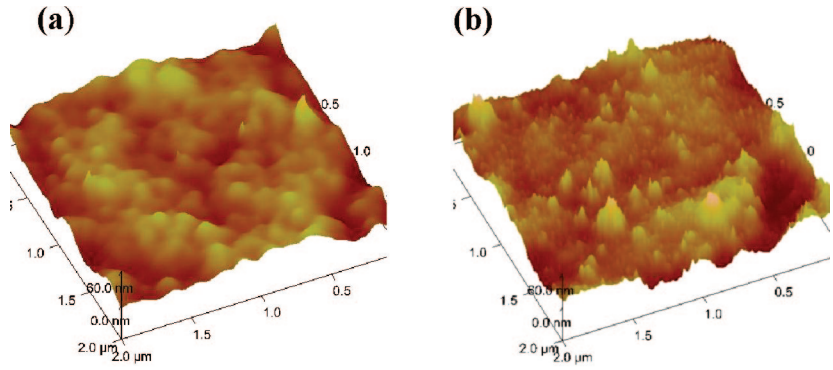


Figure 8. AFM images of (a) thin TiO_2 coating on PDMS that had been pretreated in an air plasma and (b) thin TiO_2 coating on PDMS that had been pretreated with 20% H_2SO_4.

conclude that the titania coating is relatively uniform and crack-free and maintains or improves the smoothness of the PDMS substrate. The LPD oxide film is amorphous and thus avoids discontinuities caused by grain boundaries. Moreover, once the deposition solution is filtered to remove the larger TiO_2 nucleation particles, the oxide is formed as a relatively smooth film on the surface.

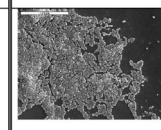
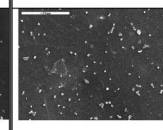
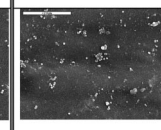
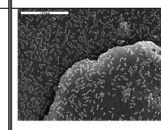
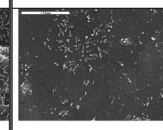
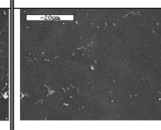
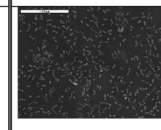
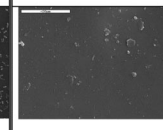
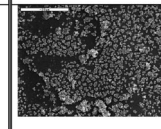
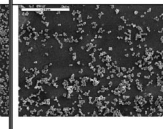
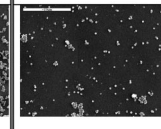
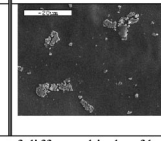
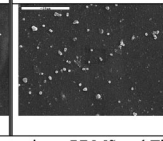
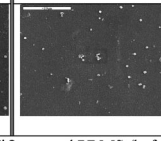
Bacteria attach to surfaces through proteins. In the case of Gram-negative bacteria these proteins assemble into pili, while for Gram-positive bacteria they do not.[46] The interaction of these proteins with the underlying surface is critical to bacterial adhesion.

The adherence of Gram negative bacteria *Acinetobacter baumannii, Pseudomonas aeruginosa*, and *Escherichia coli* to untreated PDMS, titania-coated PDMS, and titania-coated PDMS pretreated with UV irradiation was determined (Table 1, upper portion). All of these bacteria show significant buildup on PDMS, with *A. baumannii* showing such strong bacterial buildup so as to form a substantial biofilm. Bacterial adhesion is reduced by the titania coating and further reduced when the surface had been pretreated by UV irradiation.

Staphylococcus aureus and *Staphylococcus epidermidis* were examined as representatives of Gram-positive bacteria (Table 1, lower portion). *S. aureus* is shown to build up on PDMS and on titania-coated PDMS. Pretreatment with UV irradiation significantly reduces its adherence. *S. epidermidis* shows only limited adherence to all of our test samples, though it is known to adhere to other surfaces.[47,48]

The reduced bacterial adhesion on all of the titania-coated PDMS samples relative to the untreated PDMS is clear. This

Table 1. SEM Images of Different Kinds of Bacteria on PDMS and TiO_2-Coated PDMS (before and after Exposure to UV)

Bacteria	PDMS clean	PDMS + TiO_2	PDMS + TiO_2 after UV exposure
Acinetobacter baumannii			
Pseudomonas aeruginosa			
E. coli			
Staphylococcus aureus			
Staphylococcus epidermidis			

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effect was expected.[19,20,49] Moreover, the solution-deposited titania surfaces show a greater antibacterial effect for Gram-negative than for Gram-positive bacteria. This trend has not been previously reported.

The effect of UV irradiation may be related to changes in surface hydrophobicity. Exposure to UV light changes the water contact angle of the TiO_2 surface from 110° to 80°. Other studies have shown a similar reduction in the contact angle of water on TiO_2 after exposure to UV light.[50] This change in surface wetting may be what is behind the observed changes in bacterial adhesion.[51–53] It has been suggested that interfacial water, which adsorbs to polar functional groups on the substrate surface through a hydrogen-bonding network, may act as a barrier that prevents initial bacterial adhesion.[54,55]

Conclusions

Oxide thin films deposited from aqueous solution provide a powerful tool for controlling the chemical and physical characteristics of a polymer interface. For PDMS, the challenge of creating such films includes identifying conditions for priming the polymer surface, finding a suitable deposition recipe, and developing proper post-processing conditions so as to maximize the adhesion and minimize the cracking of the oxide layer. Understanding the interface between the polymer and the oxide and establishing the range of film thicknesses for which this process is effective are also essential to its success. The application of such conformal titania films on implantable biomedical devices to take advantage of their antibacterial properties is currently underway.

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