SUPERHYDROPHOBIC MODIFICATION OF ALUMINUM SURFACE: THE ROLE OF SURFACE CHEMISTRY AND STRUCTURE ON THE BIOLOGICAL INTERACTIONS

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Abstract— One of the main challenges in biomedical engineering is creating biomaterials with antimicrobial activity. The interaction of protein molecules with the surface of medical devices or prosthesis may result in the attachment of bacterial cells, which eventually triggers the colonization of cells to the biomaterial surfaces and leads to the formation of biofilm and infection. One way to prevent or postpone the biofilm formation and infection is altering the surface architecture and chemistry such that the surface becomes less prone to biofouling. Here, the surface chemistry and structure of aluminum based surfaces were modified through a cost-effective two step superhydrophobic modification method. In this method, a controlled etching process were applied to create a dual micron- and nano-scale hierarchical structures followed by a fluoro-silanization step to reduce the surface free energy. The surfaces were characterized by SEM, EDAX, AFM, FTIR, contact angel goniometry, surface free energy measurement, flow cytometry and Bradford protein assay. The effect of modification on the biofilm formation was analyzed by using microtiter plate assay using three different bacteria. The results showed that the water contact angle and surface free energy changed from 68^{o} to 163^{o} and 43.7 to 0.1mN/m, respectively. A good thermomechanical and chemical stability was observed for modified samples. They also possessed a long-term superhydrophobicity over a 4 month study period. It was also found that the BSA protein absorption capacity reduced from 3772 to 378$\mu g.ml^{-1}.cm^{-2}$ after modification. An excellent antibiofilm formation was observed for the modified samples such that, the percent inhibition of biofilm growth was found 71 percent. It was also observed that when Aluminum surface becomes superhydrophobic its bacterial adhesion becomes independent of bacterium type. This could be attributed to the fact that the nano-roughness could limit the level of contact that occurs between the substratum and the bacterium, which results in a reduction of anchor points and aggregate force of adhesion.

Index Terms— Aluminum Alloys, Biofilm formation inhibition, Hierarchical structure, Micro-nano roughness, Superhydrophobicity.
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I. INTRODUCTION

Surface engineering science is an important and advancing field for biocompatibity and biomedical application. Surface engineering technique can increase biocompatibity and biofunctionality of the surface, led to antifouling and anti-adsorption protein properties. Moreover, coating technique as a branch of surface engineering can be considered to grant a superhydrophobic coating with various beneficial properties, such as protein adsorption, biofilm formation and corrosion resistance.

Aluminum is a metal with a significant number of biomedical applications. However, its surface chemistry and morphology has made it prone for biofouling and biofilm formations and consequently infection. This has limited its utility in biomedical applications. Therefore there is still a continuing quest for surface modification of Aluminum substrate to render bio and hemocompatibility. Recently superhydrophobic modifications in biomaterial designing has shown a great potential in reducing bacterial adhesion and biofilm formation on various nonmetallic surfaces such as polyurethane, alkyltrilkoxysilane and polysiloxane[1].

Superhydrophobic modifications on Aluminum surfaces have been practiced for many non-biological applications such as self-cleaning, corrosion resistance, anti-abrasion, antifriction, robustness and anti-icing. However, there is no or very limited study on the biological interactions of superhydrophobic aluminum surfaces. Baldacchini et al.[2, 3], Jinlong et al. [4] and Han et al. treated the aluminum surface by laser , dip-coating and electrospinning[5] method in order to induce hydrophobicity. The treated surface was suitable for using in different applications, such as dental implant, biomedical device[6] and other biomedical fields[7, 8]. Surface topography as roughness and surface chemistry as wettability can be controlled using a combination of many techniques such as laser and plasma irradiation, anodizing and etching. It is reported that the combination of high surface roughness, hydrophobicity and biocompatibility makes the modified surface hemocompatible to be used for medical devices [9].
The measurement of water droplet contact angel on the substrate is easy but the definition of the surface free energy and surface wettability are complex because of various factors affected such roughness, topography and chemical surface structure [10]. Surface wettability can be modulate by modifying

surface chemistry and structure which direct the surface tensions at microscopic scale. Here, self-assembly mono layer of PFTCS polymer was functionalized by a simple method as immersing/self-assembly mono layer on the aluminum surface. A variety of techniques were used to study the effect of superhydrophobic modification on biofilm formation and biological interactions.

II. EXPERIMENTAL DETAILS

i) Materials and Procedures

Acetone, 1H, 1H, 2H, 2H-perfluorododecyltrichlorosilane (FTCS), sodium dihydrogen phosphate, disodium hydrogen phosphate, trypan blue, trypsin, bovine serum albumin (BSA), propidium iodide (PI) and nutrient broth (NB) bacterial culture media were purchased from Sigma Aldrich (Germany). Formamide, glycerin, crystal violet, ethanol 96% and absolute, Dimethyl sulfoxide, hydrochloric acid (HCl 37%), phosphoric acid 85wt. % and Coomassie brilliant blue G-250 were obtained from Merck. Three strains of bacteria containing pseudomonas aeruginosa, staphylococcus aureus and staphylococcus epidermis as biofilm former were provided from a local hospital Al Zahra hospital. MTT (thiazolyl blue tetrazolium bromide) and antibiotic and also fetal bovine serum (FBS) and Roswell Park Memorial Institute medium (RPMI) cell culture were prepared from ATOCEL and GIBCO subsequently. Commercial aluminum sheets (1cm ×1cm×1mm) were provided from local store. The preparation of aluminum surface included four steps: cleaning, etching, sealing and coating a thin layer of hydrophobic polymer on the aluminum surfaces. For modification of superhydrophobic aluminum surface, FTCS was selected due to its excellent ability to reduce surface energy. First the small pieces (1cm×1cm×1mm) were cut from aluminum plates and ultrasonically cleaned with detergents, acetone, ethanol, and deionized water to remove any impurities from Al surfaces. To alter samples surface morphology, the cleaned aluminum samples were etched by 2.5 M HCl aqueous solution for 8 min at room temperature. Subsequently, the samples were rinsed with deionized water and dried in an oven at 120 °C for 10 min. The aluminum samples were prepared by immersing samples in boiling distilled water for 15 min and subsequently dried with nitrogen. The FTCS solution was prepared by dissolving 10mg of FTCS in 10ml of absolute Ethanol. Finally, the samples were immersed in the FTCS solution (1.0 wt. %) for 48 hrs kept in room temperature and put it in an oven (100 °C) for 1 hr. In this study, ALU, ALE, ALS and ALSHP stand for unmodified, etched, sealed and surface modified (superhydrophobic) aluminum samples, respectively.

ii) Surface Characterization

In order to study the effect of surface modification on the surface morphology and roughness in micron and nano scale, a field emission scanning electron microscopy (Leo 1550 Gemini) at an accelerating voltage of 2-20 kV was used. The existence of the key elements on the created layer of the samples was evaluated, by an energy dispersive X-ray analysis (EDX) analysis (X-ray Oxford instrument). The roughness and surface topography of the ALU, ALE, ALS and ALSHP were studied by AFM test Digital Instruments Nanoscope IV. AFM images were taken in tapping mode with scan area 5×5 μm (images not shown here). Analysis by AFM showed that the each step of modification were effective towards increasing roughnesses. AFM measurement can be confirmed the SEM results of the surface and can be determined the average amount of roughness and pore size. Then samples wettability was studied by using sessile drop technique in which the contact angel of a water droplet on the sample surface was measured. Sliding angel was also measured by slowly tilting the sample stage until the water droplet starts to move [11]. The water contact angel and sliding angel were determined using Amcap v3.0 software equipped with a video camera and a tilting stage. Advancing and receding contact angles were determined by inclining the surface until the water droplet starts to roll-off [12]. The substrate angle at which the water droplet begins to move is known as sliding angle. The difference between the advancing and receding contact angles was also reported as the contact angle hysteresis which is used as the criterion for sliding properties. a clear definition [13] for advancing and receding contact angel is in that order the contact angle when water droplet has been moved at the front and meanwhile the contact angel at the rear. The mean static contact and sliding angles of 5 μl droplets on the five randomly selected regions finally were reported. In order to measure the effect of surface modification on the surface free energy changes of the samples Van Oss method was used using three different liquids of water, glycerin and formamide with known parameters as presented in Table 1.

Table 1: Acid-base parameter (van Oss)

Liquid	Surface tension (mN/m)	Dispersive component (mN/m)	Acid component (mN/m)	Base component (mN/m)
Milli-Q water	72.8	21.8	25.5	25.5
Glycerol	64.0	34.0	3.92	57.4
Formamide	58.0	39.0	23.2	23.2

iii) Biological test

Microtitre assay

To study the effect of the superhydrophobic modification on the biofilm formation and prevention, two different types of bacterial strains, Streptococcus epidermidis ATCC 35984, and Staphylococcus aureus

ATCC 25923 were selected. These bacterial strains have a strong ability of forming biofilm and are identified as nosocomial infection strains[14-16]. The bacterial strains were cultured overnight in a nutrient broth (NB) medium at 37° C with 150 rpm. The overnight bacterial suspensions were diluted with fresh and sterilized NB medium to adjust the half-McFarland standards (10^8 cfu/ml) by measuring the absorbance at 600 nm using a spectrophotometer.
The cleaned aluminum samples (ALU, ALE, ALS and ALSHP) were sterilized by autoclaving at 121°C for 20 min. Samples were immersed in the 2 ml sterile NB medium bacterial suspensions and were labeled positive control (PC). They were also immersed in the 2 ml sterile NB medium suspensions without bacteria and were labeled negative control (NC). The 24 well-polystyrene sample plate were incubated at 37° C for 24 hrs. Afterward, the samples were rinsed several times by Milli-Q water and transferred to a new polystyrene plate.
In order to stain the adhered bacteria, 2 ml of crystal violet (0.3% by volume) was added to each sample well. After 15 min incubation at room temperature, samples were washed several times by Milli-Q water to remove non-bound bacterial cells and extra stain and were transferred into a new polystyrene plate. To release the crystal violet from the bacteria cell walls, 2 ml of ethanol (95% v/v) was added to each well and after 20 min the optical density (OD) was measured at 540 nm. The results were corrected by subtracting the OD of negative controls from that of positive controls. The percentage of bacterial attachment inhibition was calculated from the below equation:

$$Percentage\ of\ inhibition\ (\%) = \left(OD_{(ALSHP-PC)} - OD_{(ALSHP-NC)}\right) / \left(OD_{(ALU-PC)} - OD_{(ALU-NC)}\right) \times 100 \quad (1)$$

Bradford protein assay

The effect of superhydrophobic modification on the proteins adsorption capacity of samples was investigated by Bradford protein assay. 1 cm^2 of superhydrophobic aluminum specimen for 4 hrs were maintained in a 1 mg/mL bovine serum albumin (BSA) solution (pH of 7.4). Then the absorbance of the solution was determined at 595 nm wavelength using a UV visible spectrometry (Biowave II spectrophotometer, United Kingdom) after removing the specimens. The amount of protein adsorbed was reported in mg/ml×cm^{-2} according to Razmjou et. al [17, 18] .

Flow Cytometry

Cell adhesive and also cells particle numbers were analyzed via flow cytometry method. The dye propidium iodide (PI) (λex 482 nm; λem 608 nm) was used for the determination of cells. Some modification were done to make this test to adaptable for aluminum samples. Here, the three different types of bacteria of S.epidermis, P.aeruginosa and S.aureus were cultured in NB medium. Stock dye solution was prepared (20 mmol/ml PI in filtrated Milli-Q water).
The aluminum samples (1×1 cm) were put in 24-wells microtiter-plate contains 2 mL bacteria suspension (10^8 cfu/ml in NB) incubated statically at 35°C for 24 hours. After incubation, aluminum samples were washed twice with Milli-Q water, meanwhile the washed aluminum samples were transformed to fresh nutrient broth media and were sonicated[19] for 30 seconds for a better detachment of adhesive bacterial cells of the samples surface. Moreover, the test was calibrated with lived and dead cells of the three stains bacteria to provide information about the location and aggregation of the dead, alieved and injured cells. The device was cleaned by Milli-Q water each time between testing different samples.

III. RESULTS AND DISCUSSION

i) Assessment of hydrophobicity

Physical and chemical properties of a surface and their synergistic effects dictate the hydrophobic or hydrophilic quality of the surface. Those properties also govern the shape of water droplets formation on the surface. The wetting property of a surface is quantified in terms of contact angel that is reported by degree. The common definition of superhydrophobicity is a surface with water contact angle (WCA) more than 150° [17] while the more widely accepted definition of superhydrophilicity is reaching the contact angle of zero within the first 5 seconds [18]. As can be seen in Fig. 2, the WCA of ALU surface is 47°and it becomes hydrophilic (<15°) after etching (ALE samples). The sealing process of the surface (ALS) leads to a superhydrophilic surface with WCA of less than 5° with 5 seconds whereas the self-assembly monolayer of FTCS on the surface (ALSHP) increased WCA to the superhydrophobic range (> 150°).
The contact angle hysteresis and sliding angle can provide valuable information regarding the quality of the surface modification [7]. A superhydrophobic surface has the self-cleaning property if it possess a small sliding angle [20]. According to Guo et al. [21] the surfaces with both large water contact angle and hysteresis (respectively above150° and 10°) is considered as the sticky superhydrophobic surface whereas it is slippery superhydrophobic if its hysteresis becomes less than 10°. As shown in Fig. 2 the superhydrophobic modification resulted to a surface with a very low affinity to water and ultra-low-adhesive property. The contact angle hysteresis and sliding angle of ALSHP samples were measured as 10° and 2° respectively. Therefore, the ALSHP samples can be considered as the slippery superhydrophobic surface which possess the self-cleaning property. It should pointed out here, that there is an argument among researchers as to whether

a surface can have WCA of above 150^o and considered as superhydrophobic which implies a strong fear of water but at the same time has large hysteresis and strong adhesion to surface[22]. For the hydrophobic surfaces as mentioned[23] hysteresis contact angle has increased when the roughness becomes lower and decreased in the large-roughness region. As discussed[24] there is an equation for the relation between contact angle hysteresis and sliding angle which contain the F factor is the amount of linear critical force for moving droplet on the substrate. Also other parameters such as 'm', 'w' and 'α' defined as the droplet weight, droplet width and sliding angle respectively. Moreover, the parameter 'ϒ' has corresponded surface free energy of the liquid at liquid-air interface. Equation 2 have been introduced receding and advancing contact angle by θ_R and θ_A:

$$F = (mg\sin\alpha)/w = \Upsilon(\cos\theta_R - \cos\theta_A) \quad (2)$$

From the (2) can be concluded that for two different surfaces with a same hysteresis contact angle necessarily do not have a same sliding angle because of the difference between amount of the weight and width parameters for various droplets. Water contact angel and sliding contact angle have an inverse relation on the superhydrophobic surfaces where is WCA is increased SA has decreased. The hierarchical structure by trapping air between liquid interface and solid surface due to have a low-sliding angle surface[25]. Also will be mentioned an equation that relieving the contact angle and sliding angle on the superhydrophobic surface with roughness. Moreover, critically high value of contact angel is not definite for low-sliding angle surface then the sliding property of droplet should have been discussed in separated means from contact angle measurement.

As mentioned before, one of the superhydrophobic modification approaches is creating a hierarchical structured modified with a low surface free energy material. Surface properties like surface roughness and energy are characteristic properties of a surface, which their changes could substantially affect the wettability of the surface [26]. Reducing the SFE can increase surface hydrophobicity while its increase enhances the surface hydrophilicity. The obtained results indicated that SFE of ALU is increased from 36.3mN.m^{-1} to 83.6mN.m^{-1} after etching, which could be due to appearance of OH groups on the surface.

Samples were studied by SEM and AFM techniques to see how the modification process changes the surface morphology of samples from micron to nano-scale. The ALU samples have the smoothest surface with the average roughness of 5nm while a roughened porous structure with hierarchical structure and multilevel roughness during the etching and sealing processes was formed. During the etching process, a microtextured surface was created, which could have a significant contribution on increasing the total roughness value of 90nm (AFM images and roughness profiles not shown here). These appearance of microplateau during etching process was also reported elsewhere[27, 28]. During the subsequent hot boiling water (sealing) treatment, two phenomena were occurred simultaneously: reduction in micron scale roughness value (from 90nm to 85nm) and appearance of nanostructured pattern. During the hot water treatment a hydrated oxide film of aluminum oxide hydroxide known as boehmite is produced[29, 30]. According to the SEM and AFM results, it seems that the fluorination treatment by FTCS molecules can reduce the surface free energy and general roughness value to 67nm, while enlarges the nano roughness value and pores on the surface.

To verify the appearance of FTCS layer EDX point analysis were performed on ALU and ALSHP samples. As can be seen in Fig. 3, the peaks of around 0.277, 1.740 and 0.677 keV are assigned to Carbon, Fluorine and Silicon. This is confirmed the presence of FTCS on the ALSHP surface whereas they were absent on the ALU sample.

In conclusion, reduction in protein adsorption decrease the biofilm formation[31]. The protein adsorption resistances of aluminum samples were studied by Bradford assay using BSA as a model protein. ALSHP sample has more resistance against the adsorption of BSA protein[32] such that ALU adsorbed BSA molecules 10.3 times more than that of ALSHP sample[33] (the graph has not showed here).

Accumulation of biofilms on surfaces that produced by microorganism causes significant health risks in human and financial losses in the medical, marine and industrial fields. Recently, superhydrophobicity has raised more attention and interests especially for its ability in reducing bacterial adhesion and biofilm formation[34]. To determine the attachment of bacteria on the coating layer on the aluminum surface, we used two strains bacteria: staphylococcus aureus and Staphylococcus epidermis which are prevalent infection-causing microorganisms and potent biofilm former on hospital medical devices such as catheters that are the most commonly used medical device[14-16]. Our result showed that the percent inhibition of biofilm growth was 71 percent. This could be attributed to the fact that the nano-roughness could limit the level of contact that occurs between the substratum and the bacterium, which results in a reduction of anchor points and aggregate force of adhesion. The reduction in the attachment of bacteria to the modified samples after 24 hr. has been reported and also high bacterial attachment found in the unmodified samples. Hence, the superhydrophobic samples show strong potential to decrease biofilm formation according to its superhydrophobicity and protein adsorption resistance feature.

Flow cytometry confirmed the number of particles and adhesive amount of bacteria cells for 24 hrs incubation time [35]. This novel assay can be applied to assess the susceptibility of the superhydrophobic coating for the bacterial attachment and then biofouling growth on the samples surface. The staphylococcus aureus is a gram positive one which was selected to investigate the effects of superhydrophobic modification steps on the biofilm formation inhabitation. Fig. 4 shows the results of flow cytometry assay for the staphylococcus aureus bacterium. As can be seen in the figure, the results indicated that the minimum particle numbers was dedicated to ALSHP sample. The number of detected particles which are correspond to the existence of cells for ALU was higher than ALSHP. According to our results, the effect of surface roughness on the mediation of bacterial cell attachment in micron and nano-scale is different.

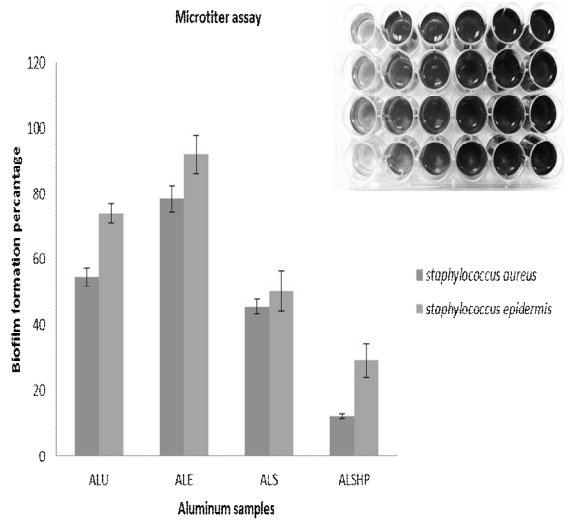


Fig. 1. Percentage of bacterial attachment for different aluminum samples, in the columns ALU, ALE, ALS, and ALSHP sample in three wells with Streptococcus epidermidis and Staphylococcus aureus and three wells control negative with fresh medium marked for ALU, ALE, ALS, ALSHP subsequently

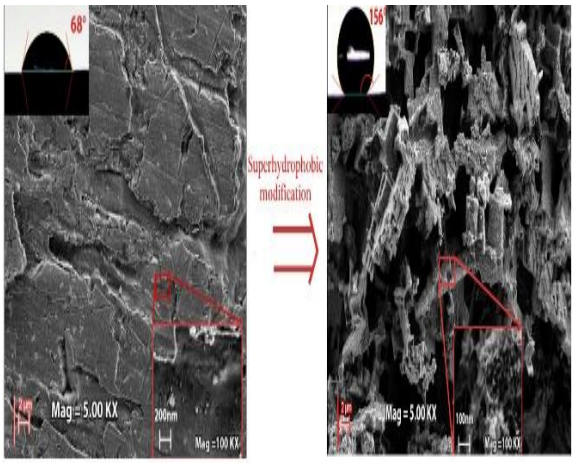


Fig. 2. SEM photographs for surface morphologies of aluminum samples before and after modification. The inset presents contact angle goniometry

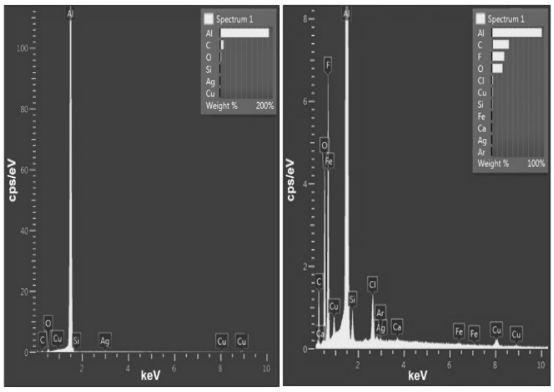


Fig. 3. EDX point ALU (left) and ALSHP (right), showing the presence of F, C, and Si on the surface after superhydrophobic modification.

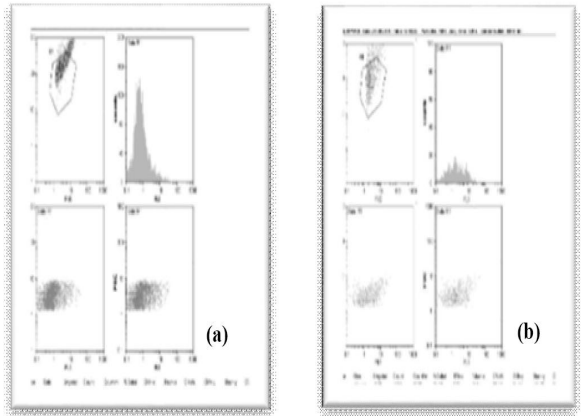


Fig. 4. Flow cytometry histogram (a) ALU sample (b) ALSHP sample for staphylococcus aureus bacterium

CONCLUSION

A hierarchical superhydrophobic nanostructured layer was successfully created through coating of FTCS molecules on the aluminum surfaces which was roughened through the etching processes. The results showed that FTCS coating significantly reduced the surface free energy and consequently resulted in a significant increase in water contact angle such that the surface wettability shifts towards superhydrophobicity. The effect of preparing micron-nano architecture on the aluminum surface was studied in terms of change in surface chemistry and structure as well as biofilm formation enhancement. A good thermal, mechanical and chemical stability was observed for the modified samples. The surface modification led to a lower protein absorption capacity, higher degree of biocompatibity and biofilm formation resistance. The systematic characterization also revealed that the contribution of surface morphological alteration on the new observed properties is more than that of surface chemistry changes.

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