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Long-Lasting Aerophilic Metallic Surfaces Underwater

Alexander B. Tesler,^{1,*} Stefan Kolle,^{2,3} Lucia H. Prado,¹ Ingo Thievessen,⁴ David Böhringer,⁴

Matilda Backholm,⁶ Bhuvaneshwari Karunakaran,⁶ Heikki A. Nurmi,⁶ Mika Latikka,⁶ Lena

Fischer,⁴ Shane Stafslien,⁵ Zoran M. Cenev,⁶ Jaakko V.I. Timonen,⁶ Mark Bruns,¹ Anca

Mazare,^{1,7} Ulrich Lohbauer,⁸ Sannakaisa Virtanen,¹ Ben Fabry,⁴ Patrik Schmuki,^{1,9} Robin H.A.

Ras,^{6,10} Joanna Aizenberg,^{2,3} Wolfgang H. Goldmann^{4,*}

- ⁵ Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND 58102, USA.
- ⁶ Department of Applied Physics, School of Science, Aalto University, P.O. Box 15100, Espoo FI-02150, Finland.
- ⁷ Advanced Institute for Materials Research (AIMR), National University Corporation Tohoku University (TU), Sendai 980-8577, Japan.
- ⁸ Department of Operative Dentistry and Periodontology, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91054 Erlangen, Germany.
- ⁹ Regional Centre of Advanced Technologies and Materials, Palacky University, Listopadu 50A, 772 07 Olomouc, Czech Republic.
- ¹⁰ Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Espoo FI-02150, Finland.

*Corresponding authors. E-mail: alexander.tesler@fau.de, wolfgang.goldmann@fau.de

Abstract: Aerophilic surfaces immersed underwater trap air, so-called plastron. To date, plastrons

have been reported to be impractical for engineering applications underwater due to their short

¹ Department of Materials Science and Engineering, Institute for Surface Science and Corrosion WW4-LKO, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany.

² Wyss Institute for Biologically Inspired Engineering, Harvard University, Cambridge, MA 02138, USA.

³ John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.

⁴ Department of Physics, Biophysics Institute, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91052 Erlangen, Germany.

lifetime. Here, we describe aerophilic titanium alloy (Ti) surfaces with extended plastron lifetime, conserved for months underwater. Long-term stability is achieved by the formation of highly rough surfaces through electrochemical anodization, combined with low surface energy coating, made by a fluorinated surfactant. Such aerophilic Ti surfaces drastically reduce adhesion of blood, and when submerged in water, prevent adhesion of bacteria and marine organisms such as barnacles, and mussels. Applying thermodynamic stability theories, we describe a generic strategy for achieving long-term stability of plastron on aerophilic surfaces for demanding and hitherto unattainable applications.

Introduction

Wetting describes the ability of liquids to maintain contact with a solid surface, a phenomenon that is ubiquitous in nature.¹ In engineering and medical applications, however, contact of solid surface with water can result in undesired phenomena such as corrosion, chemo- and bio-fouling,² having an extremely negative impact on economics, health, and the environment.^{3,4} Hence, the control of wetting on solid surfaces is key to mitigating its detrimental effects. Although wetting is a macroscopic process, it is sensitive to surface properties on a molecular scale. Thus, wetting is greatly influenced by surface topography. High surface roughness in combination with low surface energy materials results in the formation of non-wettable, so-called superhydrophobic surface energy chemistry can trap air in between the protrusions while submerged in water, termed plastron, also called aerophilic surfaces (APhS).⁶ SHS have been researched to overcome wetting challenges for decades;⁷ yet, they are still rarely employed in engineering applications mainly due to two drawbacks. Firstly, highly textured rough surfaces are mechanically weaker than their analogue smooth surfaces and, thus are easily abraded.⁸ This drawback of SHS was recently

addressed by various strategies.⁸⁻¹¹ Secondly, a much less solved drawback is that the non-wetting characteristics degrade over time due to the metastable performance of plastron, which arises from the co-existence of different energy states.^{12,13} This metastable performance is even more crucial when APhS are submerged in water, and the air that is trapped between the protrusions disappears over time.¹⁴ As a result, the long-term stability of such surfaces underwater has been considered insufficient for many engineering applications, most notably for prevention of biofouling.¹⁴ Thus, the long-term stability of plastron remains the "Achilles heel" in the implementation of SHS/APhS technology,¹⁵ while in biology, several species have evolved unique approaches to maintain entrapped air underwater for long periods.¹⁶⁻¹⁹ Furthermore, it is even more challenging to produce mechanically robust SHS/APhS with stable plastron by a facile, inexpensive, and scalable process.

Here, we report aerophilic surfaces formed on the widely used titanium alloy (Ti6Al4V, referred to as Ti-APhS), resulting in unprecedented plastron stability exceeding 208 days of continuous immersion underwater. Our Ti-APhS are produced through an industry-standard electrochemical anodization technique followed by the modification of a commercially available fluorinated surfactant. We demonstrate that Ti-APhS are extremely blood repellent and drastically reduce or altogether prevent the adhesion of bacteria and marine organisms such as mussels and barnacles. The resulting surface roughness and interfacial energy give rise to a thermodynamically stable aerophilic regime as predicted by existing theories.²⁰⁻²² This work provides experimental evidence and confirmation of the theory, demonstrating that long-lasting trapping of air on artificially-made SHS is feasible for a wide application spectrum.

Results and discussion

Physicochemical characteristics of Ti-APhS

Ti-APhS were prepared by the electrochemical anodization of Ti6Al4V alloy. The anodization cell consists of stainless steel used as a counter electrode, Ti alloy as a working electrode, and the aqueous solution of NaOH/H₂O₂ as electrolyte. Ti substrates were used as received without any pre-treatment other than cleaning (see Materials and Methods). To obtain TiO₂ layer of high roughness, two concurrent reactions should occur: (i) the electrochemical oxidation of the metal surface forming an oxide layer, and (*ii*) the chemical dissolution of the formed oxide in the same electrochemical environment to increase porosity and to create nanoscale roughness (Fig. S1, and Section S1).²³ Scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM) of Ti-APhS confirm the hierarchical structure of randomly oriented, irregular-shaped micrometer-scale protrusions with a subtle, nanoscale rough surface of anodized TiO₂ (Fig. 1a-b, and Fig. S2-3). The bare and as-anodized Ti substrates are shown in Fig. S4-5. X-ray diffraction (XRD) spectroscopy and high-resolution transmission electron microscopy (HR-TEM) confirm the formation of a rough amorphous TiO₂ layer (Fig. S6). The APhS coating can be equally created on flat and curved Ti substrates such as sheets, foils, rods, and coils (Fig. 1c-d).



Fig. 1. Physicochemical characteristics of Ti-APhS. High-resolution top-view (a) scanning electron microscopy (increasing magnifications), and (b) atomic force microscopy images of Ti-APhS. (c-d) Digital images of Ti-APhS prepared on sheets (c) and rods (d) demonstrate mirror-like reflectance underwater. The Ti-APhS rod of 2 mm in diameter. (e) EDS and (f) high-resolution X-ray photoelectron spectroscopy C 1s spectra of bare, as-anodized, and Ti-APhS. (g) Sliding friction force as a function of drop contact area diameter (differently sized water drops) on Ti-APhS, probed on both sides of the samples and obtained by the micropipette force sensor. The abbreviations S_1 and S_{1B} represent the front and back sides of sample 1 (of 3), respectively.

A water drop, deposited on the as-anodized Ti substrate, wets it completely exhibiting water contact angle (WCA) of 0° , *i.e.*, superhydrophilic (**Movie S1**). Superhydrophobic/aerophilic Ti (Ti-APhS) surfaces were obtained by immersion of the as-anodized Ti substrates in a container of 1 wt.% commercially available phosphate-ester fluorinated-alkyl chain surfactant (FS) solution under ambient conditions.¹¹ It is worth noting that poly- and perfluoroalkyl substances are subject to regulations due to their chemical stability leading to bioaccumulation.²⁴ Therefore, to minimize the fluorinated compounds waste, the FS solution has been used numerous times for a period of >3.5 years without showing any signs of degradation in its coating performance. Energy-dispersive X-ray spectroscopy (EDS) (**Fig. 1e** and **Fig. S2-3**) and X-ray photoelectron spectroscopy (XPS)

(Fig. 1f and Fig. S7-8) show the typical peaks attributed to bare, as-anodized, and Ti-APhS confirming the binding of the surfactant to the anodized TiO_2 . Interestingly, the as-anodized Ti samples do not show an adventitious carbon peak even after months of aging in an ambient atmosphere (Fig. 2f), as usually occurs on TiO_2 nanostructures due to the adsorption of contaminating molecules from the air.²⁵

The wetting characteristics of Ti-APhS were investigated. Ti-APhS exhibit mirror-like uniform reflectance underwater due to the plastron (Fig. 1c-d), in contrast to their as-anodized counterparts that are non-reflective (Fig. S9). They are ultra-slippery with an apparent WCA of $170.0^{\circ} \pm 8.6^{\circ}$ and a sliding angle of $0.7^{\circ} \pm 0.3^{\circ}$. The data was obtained by a conventional goniometer. However, the measurements were not reliable simply because water droplets tend to roll off quickly on Ti-APhS (Movie S2). Also, it has been demonstrated that for ultra-slippery surfaces, a significant change in the measured WCA values occurs, if the fitting baseline shifts even by a single pixel.²⁶ Here, alternate approaches were applied to confirm and estimate the ultraslipperiness of Ti-APhS with better precision. A micropipette force sensor (MFS) that measures the friction force of water droplets on ultra-slippery SHS (Fig. 1g, Fig. S10a, and Movie S3).²⁷ and oscillating droplet tribometer (ODT) that measures the friction force between the SHS and the test droplet over a centimeter-scale range,²⁸ confirm ultra-slipperiness of Ti-APhS. We further compared Ti-APhS to the state-of-the-art SHS, and the dimensionless friction force measurements set Ti-APhS among the most slippery of the examined engineering SHS, demonstrating uniformity over the entire sample area (Fig. S10b).

Typically, non-wettable surfaces are described by an apparent contact angle and contact angle hysteresis (CAH). However, this approach is not accurate enough to describe ultra-slippery surfaces and, particularly, their plastron stability underwater. Thus, another methodology should be applied to characterize accurately the wetting regime of such materials. This was proposed by *Lafuma* and *Quéré* for SHS,²¹ and calculated theoretically by *Marmur* for aerophilicity underwater.^{20,22} In both approaches, every non-wettable surface should be described as follows: (*i*) the Young's contact angle estimated by measuring the most stable contact angle on a smooth substrate of the same hydrophobic origin, (*ii*) surface roughness (the actual over projected surface area ratio), and (*iii*) the solid-liquid area fraction (actual contact area between water and solid surface - pinning points). To be useful for real engineering applications, such SHS/APhS should also be mechanically robust.¹³

Ti-APhS were examined by both approaches to characterize their wetting regime. Initially, we estimated the most stable WCA (θ) on FS-modified Ti alloy substrates, polished to a mirror-like state (p-TiHS). Note, it is impossible to polish metallic samples down to atomic resolution. The roughness of p-TiSH was evaluated by laser confocal microscopy and found to be 1.005 ± 0.001 (**Fig. 2a-b**). The most stable WCA is the apparent CA related to the lowest Gibbs energy for a given system,²⁹ where the CAs are believed to approach the Young's values. Yet, there is no common method to measure the most stable CA precisely, while a measurable CA could be any value between advancing and receding CAs, *i.e.*, the highest and the lowest metastable apparent CAs. Here, the most stable WCA of the p-TiHS is located between the advancing ($\theta_{adv} = 124.4^{\circ} \pm 0.8^{\circ}$) and receding ($\theta_{rec} = 82.9^{\circ} \pm 4.0^{\circ}$) CAs (**Fig. 2c** and **Fig. S11.1**). For instance, when a water droplet was deposited on p-TiHS, the apparent WCA was 119.3° ± 2.6°. For comparison, the advancing and receding WCAs on the FS-modified 100-nm-thick SiO₂ on Si wafer with nanoscale roughness were 122.6° ± 1.4° and 97.0° ± 3.6°, respectively (**Fig. S11.1p-i**).

The surface roughness (*r*) of Ti-APhS was obtained using a laser confocal microscope, and further confirmed by atomic force microscopy (AFM), and an optical confocal white light sensor profilometer (**Fig. 2d** and **S11.2**). While all the techniques confirm similar roughness within standard deviation measurements, the lowest value of 2.388 ± 0.35 was obtained by AFM. Finally,

we measured the solid-liquid area fraction (φ_s) using bright-field reflectance microscopy, while Ti-APhS were immersed underwater. The solid-liquid area fraction was found to be 0.0054 ± 0.0047 meaning that the plastron covers ~99 % of the surface (**Fig. 2e** and **S11.3**). Cross-sectional confocal microscopy images confirmed the existence of plastron (**Fig. 2f**).



Fig. 2. Quantifying the wetting regime of Ti-APhS. (a) Top-view laser confocal, (b) scanning electron microscopy images, and (c) corresponding advancing and receding CAs measured on p-TiHS. The image in (c) is a composite from advancing and receding CA measurements. Inset in (a) is a digital image of the polished FS-modified Ti alloy with mirror-like reflectance. (d) Typical 3D reconstruction image of Ti-APhS roughness obtained by AFM. (e) A typical bright-field reflectance microscopy image of Ti-APhS underwater, and (f) a confocal cross-sectional image of plastron on Ti-SHS underwater. (g) The apparent WCA ($\cos(\theta^*)$) as predicted by the Wenzel and

C-B models as a function of the most stable WCA (cos (θ)) based on the solid-liquid area fraction on Ti-APhS. The stable C-B wetting regime changes at the critical contact angle (cos (θ_c)) to a stable Wenzel or meta-stable C-B regime. The green area represents the possible wetting regimes of Ti-APhS measured on p-TiHS and compared to FS-modified Si/SiO₂ wetting system (Si/SiO₂/FS, yellow area). (**h**) Minimum roughness (r_{min}), measured by AFM, optical profilometer, and laser confocal microscopy on Ti-APhS, required for a stable plastron underwater for $\varphi_{s_max} =$ 0.011 (corresponding to the upper limit of liquid-solid area fraction) as a function of the most stable WCA (θ).

Wetting of liquids on rough solid surfaces is described in terms of the balance of interfacial Gibbs energies of solid, liquid, and vapor phases. Two wetting regimes, *i.e.*, Wenzel (homogeneous or fully wetted, also known as pinning regime) and Cassie-Baxter (heterogeneous or composite surface of vapor and solid, *i.e.*, aerophilic, also known as slippery regime), may coexist on the same substrate (Fig.2g, blue and dashed red lines), while the relative value of Gibbs energy minima and the barrier between them depends on the chemical nature of the surface, the particular surface topography, and the wetting liquid.^{13,22} It is generally accepted that plastron on artificial SHS is metastable. It means that a transition from Cassie-Baxter to Wenzel wetting regime often occurs and, in particular, underwater.¹² To adequately evaluate wetting regime as well as the stability of plastron underwater, we applied methodologies suggested by Lafuma and Quéré,²¹ and Marmur.^{20,22} In the first case, the critical (threshold) contact angle (θ_c) between the two wetting regimes was calculated from $\cos(\theta_c) = (\varphi_s - 1)/(r - \varphi_s)$ and was found to be $\theta_c =$ 114.5° ± 4.5° (Fig. 2g).²¹ Any value of Young's WCA higher than θ_c indicates the formation of the stable Cassie-Baxter wetting regime, while SHS with lower than θ_c values may demonstrate either stable Wenzel or metastable Cassie-Baxter wetting. Based on the calculations, while considering the limitations of the most stable CA measurements, it suggests that Ti-APhS may exhibit a stable C-B wetting regime (Fig. 2g, green rectangle area). To validate the plastron stability underwater, calculations suggested by *Marmur* were applied, where thermodynamic

equilibrium and stability conditions to minimize the solid-liquid contact area were formulated.²⁰ It was postulated that for a sufficiently high roughness ratio (r_{min}) , plastron is feasible and thermodynamically stable. The results are presented in Fig. 2h, for the upper limit of measured φ_s for Ti-APhS, *i.e.*, 1.1 % of the solid-liquid contact area. This methodology also demonstrates that the obtained roughness of Ti-APhS as well as the hydrophobic nature of the surfactant may raise Ti-APhS above the minimum roughness condition required for stable plastron underwater (for further discussion see Section S11). The aerophilic lifetime of Ti-APhS was evaluated as follows: (*i*) Ti-APhS trap air bubbles for more than 208 days of continuous submersion, and the experiment is still ongoing without showing any sign of degradation (Fig. S11.4 and Movie S4). (ii) While submerged at 50 cm depth, Ti-APhS demonstrated an aerophilic Cassie-Baxter regime for 14 days, while after 67 days, ~10 % of the area had transformed into the Wenzel regime (Fig. S11.5 and Movie S5). The latter is 36-times longer than any *state-of-the-art* APhS submersed at 50 cm depth (considering at least 50 % plastron failure) (Table S2). Plastron lifetime of 30 days was previously reported as ultra-stable,³⁰ while periods longer than 50 days were defined as infinite plastron lifetime.³¹ (*iii*) Ti-APhS was floating on water for 133 days due to plastron, while without plastron the sample sank immediately (Fig. S11.6). These results demonstrate that APhS with sufficient roughness can effectively trap and hold plastron underwater for months.

The excellent water repellency of Ti-APhS is attributed mainly to stable plastron. Thus, to be employed in engineering applications and, particularly, underwater, mechanical robustness is vital. The mechanical durability of Ti-APhS was studied by water jet impact (70 psi), bending, linear,⁹ and sand³² abrasion mimicking harsh outdoor conditions. Ti-APhS preserve their wetting characteristics under hot and cold water jets (the calculated water jet force was 8.98 N equivalent to ~900 g of mass impinging the surface) (**Movie S6**), bending, twisting (**Movie S7**), and sand abrading by hard and heavy particles (**Fig. S12** and **Movie S8**). Ti-APhS maintain a contact angle

higher than 150° after 20 cycles of linear abrasion obtained by a stainless steel block, although the sliding angle increases (**Fig. S13**). A combination of a chemically bonded (intrinsically) TiO₂ with irregularly shaped amorphous protrusions minimize the propagation of damage over a large area, allowing superb resistance of Ti-APhS to counteract compressive and tensile stresses.¹¹

Antifouling performance of Ti-APhS

Blood repellency

Blood is a highly challenging liquid to repel due to its tendency to activate intrinsic hemostatic mechanisms, induction of coagulation, and platelet activation upon contact with a foreign body.³³ Imbalanced activation of coagulation influences the formation of blood clots (thrombogenesis), which can deter blood flow exposing tissues to ischemia and infarction. Blood-repellent SHS aim to reduce thrombogenicity of blood-contacting devices and implants by minimizing their contact with blood. The main challenge is the long-term stability of the slippery wetting regime under physiological conditions as plastron tends to disappear.

Since the Ti alloy used in this study is the most applied material for implants, we investigated blood repellent characteristics of Ti-APhS by immersing it in a container with blood (**Fig. 3**). As shown in **Fig. 3a-c**, the Ti-APhS has an apparent blood CA of $169.6^{\circ} \pm 6.4^{\circ}$ and CA hysteresis of $\sim 14^{\circ}$ demonstrating very low blood adhesion (**Movie S9**). Sessile blood drops on Ti-APhS can be simply removed by a paper wipe, leaving behind a clean surface free of blood traces (**Fig. 3d** and **Movie S10**). We performed sequential immersion of Ti-APhS in blood 99-times holding it immersed for 1 s during every cycle (**Fig. 3e**). The bare Ti surface (control) was entirely covered by blood after the first immersion (**Fig. S14a-b** and **Movie S11**). Here, due to the preparation process, Ti-APhS are evenly coated on both sides and edges. Potentiostatic current transients confirmed the continuity of plastron (for details see **Section S15, Fig. S15 and Movie S12**). Ti-

APhS immersed 99-times was completely free of blood on both sides and the edges (**Fig. 3e and Fig. S14c-d**). **Fig. 3f** demonstrates blood drops rolling off Ti-APhS after 99-times of immersion, confirming the stability of plastron (**Movie S13**). For comparison, FS-modified SHS aluminum displayed similar wetting characteristics, but of different morphology and mechanical robustness, lost plastron after only a few seconds of exposure to blood (**Movie S14**).



Fig. 3. Blood repellency of Ti-APhS. CA of fresh blood on (**a**) as-anodized and (**b**) Ti-APhS. (**c**) Advancing and receding CA measurements on Ti-APhS. Inset images: droplet shape during increasing and decreasing blood droplet volume. (**d**) Snapshot digital images of the blood droplet wiped off from Ti-APhS by paper tissue. (**e**) Digital images of Ti-APhS before, during, and after 99-times of immersion in fresh blood. (**f**) Blood dripped on Ti-APhS shown in (**e**). (**g-h**) Ti-APhS after immersion in fresh blood for (**g**) 10 s and (**h**) 60 s. (**i-j**) Still digital images of the sample immersed in fresh blood for 3,600 s (**i**), followed by a brief rinse in water (**j**).

The blood repellent longevity of Ti-APhS was estimated by subsequent immersion in a container with blood at various times (**Fig. 3g-i**). Ti-APhS was completely free of blood after 0.8 h of immersion, while after 1.8 h, several small blood spots were observed and removed by a brief rinse in water (**Fig. 3j**, and **Fig. S14e-g**). The unique blood repellency of Ti-APhS is attributed to the synergy between plastron stability (enabled by surface topography and chemistry) and mechanical robustness.

Bacterial repellency of Ti-APhS

Due to the rise in human life expectancy, metallic implants made of Ti6A14V have become common practice in orthopedic/dental surgeries.³⁴ Nevertheless, the implant surfaces are prone to bacterial fouling and biofilm formation, which are difficult to be removed even by antibiotics that can potentially lead to severe postoperative surgical site infection.³⁵ Biofilms grow on a solid surface covered by fluid;³⁶ therefore, reducing the contact between a solid surface and fluid containing bacteria, *e.g.*, such as APhS, is expected to affect biofilm formation and growth. We studied bacterial adhesion by exposing Ti-APhS to green fluorescent protein (GFP) expressing *Escherichia coli (E. coli*), while bare, as-anodized (superhydrophilic), and bare-FS-modified (hydrophobic) substrates were used as control. It has been shown that *E. coli* flagellar filaments aid adhering to wetted rough surfaces enabling them to reach into crevices and produce a dense, fibrous network within a short time.^{14,37} Live confocal microscopy revealed a steady increase in

bacterial coverage on all control surfaces, but to a much lesser extent on Ti-APhS (**Fig. 4a-b**, **Fig. S16** and **Movie S15**). Sliding time window analysis was applied to identify non-motile bacteria, as opposed to floating bacteria captured on a single frame. This revealed a consistent increase in surface coverage of the controls, while Ti-APhS showed hardly any bacterial accumulation (**Fig. 4a**). Quantification of bacterial surface coverage confirmed a similar increase on all control substrates, while Ti-APhS showed only a small increase (**Fig. 4b**).



Fig. 4. Bacterial repellence of Ti-APhS. (a) Time-lapse images of non-motile live GFP-expressed *E. coli* on bare, as-anodized, and Ti-APhS. Scale bar: $10 \mu m$. (b) Surface coverage on the samples shown in (a). Line width indicates mean \pm standard deviation measured from three independent biological replicates. (c) Images and (d) surface coverage of non-motile bacteria on samples shown

in (a) after 4 h of bacterial exposure and subsequent washing (** indicates p < 0.01 obtained by a two-sided student t-test). Scale bar: 10 μ m.

To examine whether the non-motile *E. coli* represents surface-adherent bacteria rather than bacteria trapped in the developing biofilm, all examined surfaces were washed and analyzed using a short sliding time window (**Fig. 4c**). As demonstrated, bacteria cover a large portion of the control samples even after washing, confirming that our assay showed adherent bacteria. In contrast, the few bacteria covering Ti-APhS after the exposure period were removed almost completely after washing (**Fig. 4d**). This demonstrates the inability of bacteria to infiltrate and adhere to Ti-APhS due to the stable plastron caused by a very low liquid-solid contact area. Furthermore, these data confirm that (*i*) prolonged immersion of rough surfaces underwater encourages bacterial adhesion during long-term exposure, (*ii*) FS surfactant is generally non-toxic to bacteria, allowing comparable biofilm formation as demonstrated on bare Ti surfaces, and (*iii*) Ti-APhS with stable plastron retard bacterial biofilm formation of *E. coli*.

Marine anti-biofouling performance of Ti-APhS

Preventing the adhesion of marine organisms is considered a particularly challenging application for non-adhesive surfaces due to the short-life of plastron (**Table S2**).¹⁴ Here, we assess the protective nature of plastron stability underwater of Ti-APhS when exposed to several most challenging marine organisms such as mussels, and barnacles, so-called hardfoulers. This is because marine mussels are able to attach firmly to wet organic and inorganic surfaces by secretion of mussel foot proteins,³⁸ while barnacles secrete a multi-protein complex called bio-cement that hardens at the adhesive joint and is insoluble in water.³⁹ The marine biofouling setups and the results are summarized in **Fig. 5**. As shown, mussel (*Geukensia demissa*) adhesion was completely prevented by Ti-APhS over the 3-day experimental immersion period (**Fig. 5a-b**). Adult barnacle

(*Amphibalanus amphitrite*) re-adhesion occurred on Ti-APhS; yet, the adhesion strength of the barnacles was markedly lower on Ti-APhS than on untreated controls and comparable to the fouling release treatment Intersleek 700, *i.e.*, commercial anti-biofouling paint, over a 14-day experimental immersion period (**Fig. 5c-d**). These results show that Ti-APhS prevent biofouling over an extended period of submersion due to long-lasting stable plastron, even in the presence of macrofouling organisms that use proteinaceous adhesives (mussels) and bio-cement (barnacles). These results further suggest that FS surfactant is non-toxic to marine organisms showing, *e.g.*, similar re-attachment of barnacles compared to non-toxic commercial paints.



Fig. 5. Marine anti-biofouling characteristics of Ti-APhS. (a) Mussel (*Geukensia demissa*) adhesion assay determining forces required to pull the mussel from the substrate. (b) Mussel adhesion strength on bare, as anodized (superhydrophilic), Ti-APhS, and PU (control) samples. The blue star indicates that mussel failed to adhere to the coating surface. (c) Adult barnacle (*Amphibalanus amphitrite*) reattachment assay. (d) Adult barnacle adhesion strength on bare, as

anodized (superhydrophilic), Ti-APhS, polyurethane (PU, control), and commercial antibiofouling paints (Intersleek 700, 900, 1100SR). The blue star indicates that barnacles failed to readhere to the coating surface; red stars indicate barnacle shell fracture and/or base plate breakage during the test and remained on the coating surface, *i.e.*, coating failure.

Conclusions

Despite intensive studies of superhydrophobic (aerophilic) surfaces in the past, the focus of research needs to be adjusted to develop long-life stable aerophilic surfaces underwater. While mechanical robustness of SHS has recently been demonstrated, the metastability of plastron has been addressed insufficiently. A transition from a composite wetting (C-B) to a fully-wetted (W) regime within a relatively short time is primarily responsible for the failure of SHS/APhS in general and in particular underwater, promoting undesirable processes such as corrosion, chemoand bio-fouling. Water contact angle and hysteresis, two of the most commonly reported material properties, do not provide direct information on plastron stability, making it difficult to predict the aerophilic performance of surfaces underwater. Therefore, characteristics like surface roughness, the solid-liquid area fraction, and the most stable contact angle measured on the smooth surface of the same hydrophobic origin are vital parameters to shed light on whether the developed APhS are in a stable or metastable slippery regime. Despite decades of research, the study of aerophilic surfaces still needs advanced characterization methodologies to obtain and ensure unambiguous interpretation of all aforementioned parameters. As we show, by determining plastron stability, it is possible to extend the APhS performance underwater to months, impeding attachment of blood, bacteria, and marine organisms. Our Ti-APhS demonstrate similar marine biofouling retention compared to state-of-the-art anti-biofouling commercial paints. The simple and scalable preparation of uniformly rough Ti6Al4V alloy surfaces of various geometries using inexpensive material and industry-used electrochemical techniques, together with a facile approach for

lowering surface energy and mechanical robustness, all these together make this method implementable, *e.g.*, for biomedical applications. Finally, our approach to create highly rough Ti surfaces with well-defined uniform morphology may serve as an excellent scientific model for investigating plastron stability to conserve aerophilicity over months up to years for highly challenging marine applications.

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