

SUPERHYDROPHOBIC SURFACES FOR APPLICATIONS IN SEAWATER

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ABSTRACT

Shipping, oil industry and marine aquaculture, but also cooling heat-exchange systems for desalination and power plants, undergo detrimental effects induced by corrosion, biofouling and friction reduction. Highly water repellent or superhydrophobic coatings are regarded as key solution for retarding, if not preventing, physico-chemical phenomena at the base of these effects.

In this work, the authors have reviewed the recent literature focusing on superhydrophobic technology and application in various fields dealing with seawater from the protection of boat and ship hulls to the use of seawater in industrial plants, trying to evidence the state of the art and to describe possible future directions with open fields and questions.

Keywords: Superhydrophobicity, fouling, protection, marine environment

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INTRODUCTION

Many technological applications dealing with seawater have to face degradation phenomena when the seawater interacts with materials (metallic or not) in a large variety of operative/environmental scenarios. Large-scale technological fields like shipping, oil industry and aquaculture (working directly in the sea), and cooling heat-exchange systems for desalination and power plants (exploiting seawater near, off-shore) undergo detrimental effects induced by corrosion, biofouling and friction reduction.

As reviewed by Salta et al. [Salta, 2011], whatever surface (natural or artificial) immersed in seawater, is affected by biofilm attachment and biocolonization, featured, in most cases, by a large variety of microfoulers and macrofoulers. Concerning on biofouling developing on hulls, the most important cost is the enhance of the fuel consumption linked to frictional drag [Schulz, 2011], penalizing the hydrodynamic performance of ship hull surfaces. In order to figure out the enormous economical impact depending on fouling on ship hulls, the cited author estimated \$56 million per year for the entire class of DDG-51 naval ships.

In the story of remediations devoted to remediate on biofouling induced damages, a very important milestone is located in 1974, when self-polishing copolymer (SPC) paints were introduced [Callow, 2002]. The SPC system, dissolving away during normal vessel operation and releasing tributyltin (TBT), was extremely successful due to its non-target toxic action against settling fouling organisms. In turn, the very significative environmental drawbacks drove towards their ban in 2008 [Gipperth, 2009]

Therefore, any kind of innovation allowing to mitigate or solve the above mentioned criticisms connected to seawater interactions, coniugating economical and green features, represents the right direction where to spend energies and efforts.

In this sence, a very intriguing possibility is represented by the superhydrophobic coating technology, for which corrosion [Xu, 2011; Wang, 2011; Liu, 2013], and foul [Genzer 2011; Crick 2011; Sousa 2011] control properties are being studied more and more intensively in recent years. The most important challenge is represented by the variety of situations encountered in the seawater environments/applications, and by the necessity to guarantee life time performances and, where necessary, easy maintenance interventions.

In this review, the application of the superhydrophobic technology to the protection of boat and ship hulls is mainly considered together with the use of seawater in industrial plants, evidencing the directions touched by the researches and evidencing open fields and questions where we think it will be necessary to spend future efforts.

SUPERHYDROPHOBIC SURFACES

Learning from nature, one of the first lessons are the self-cleaning properties of Lotus leaves, under investigation in the last decades for their particularly strong water repellency of its unique structure with highly hydrophobic character.

The terms superhydrophobic or ultrahydrophobic refer to low energy surfaces with a water contact angle (CA) greater than 150° and since the introduction of the idea of the Lotus effect [Barthlott and Neinhuis, 1997; Neinhuis and Barthlott, 1997], many investigations introduced techniques to enhance and exploit the self-cleaning properties of solid surfaces, mostly by controlling the roughness and topography of low energy surfaces (Fig.1).

The exploitation of structural properties of plant or animal surfaces have generated new approaches like biomimetics where, starting from micro or submicroscopical observations, structures with specific tailored features have been created with large impact in terms of application in a wide range of basic research and industrial fields.

The Lotus leaves structure has been studied in detail by Marmur [Marmur, 2003; Marmur, 2004] by electron microscopy, showing a 2D roughness in leaf appendixes of several micrometer in size and covered with nano-micro sized wax crystals.

The investigation on birds and insects wings or beetle shields [Wagner, 1996; Zhail, 2006], together with different kinds of plants leaves, were already present in the works of Wenzel [Wenzel, 1936; Wenzel, 1949] and later [Cassie and Baxter, 1944], bringing the observation that such a strong hydrophobic effect rises from coupling a micro- and nano-patterned surface with a particular geometry with a coating of natural organic compounds of different nature.

The roughness effect on the wettability properties of a solid surface have been interpreted by the models of Wenzel and Cassie-Baxter.

Assuming the liquid filling the space between the protrusions on the surface, the Wenzel's approach correlates the apparent contact angle θ' and thermodynamic contact angle θ as

$$\cos\theta' = r \cos \theta, (1)$$

where r (roughness factor) is the ratio between the true surface area and its horizontal projection.

Cassie and Baxter introduced the idea that the surface traps air in the hollow spaces of the rough surface, interpreting the superhydrophobicity as following:

$$\cos \theta' = f_{LS} \cos \theta - f_{LV} (2)$$

where f_{LS} is the fraction of liquid area in contact with the solid and f_{LV} is the fraction of liquid area in contact with the trapped air ($f_{LS} + f_{LV}=1$).

Contact angle hysteresis can discriminate the two states. At larger hysteresis they can be regarded as belonging to the Wenzel's one with the liquid entering the surface grooves, while, at smaller

hysteresis values, the Cassie-Baxter surface can be regarded as composed by a pillar-like structure supporting the liquid and reducing the available area.

The importance, the role and the structure of air pockets trapped in the nano surfaces will be later discussed.

Onda and co-workers [Onda, 1996] created “artificial” superhydrophobic surfaces by combining micrometer and nanometer-scale roughness with low surface energy in a nonhomogeneous wetting regime (Cassie-Baxter regime).

Bico *et al.* [Bico,1999] for example showed that a significant decrease of resistance to liquid drainage can be expected on such surfaces with a small contact with water, but also an inhibition of various phenomena, like adhesion and oxidation, related to physicochemical interactions in an aqueous environment.

The presence of low surface energy and high roughness at nanometric scale was also assessed by Öner and McCarthy [Öner, 2000] and by Feng *et al.* [Feng, 2002] putting in evidence the key role played by surface roughness as an amplifier of the hydrophobicity in natural and artificial substrates by combining geometrical and chemical characteristics.

Despite a substantial increase in the degree of hydrophobicity has been for a long time recognized due to an increase of surface roughness of a hydrophobic solid substrate, in [Feng, 2003] we found that such effect can be proved starting from an amphiphilic polymer coating, although these surfaces are generally fabricated by combining a suitable surface roughness with low surface energy materials.

Regarding the roughness scale some authors [Scardino, 2009] have more recently investigated fouling resistant solutions by nano-engineered superhydrophobic surfaces integrating hydrophobic materials with nanoscale roughness.

High water contact angles ($>150^\circ$) and comparatively low hysteresis ($<10^\circ$) were found in the superhydrophobic coatings, different by chemical composition and architecture.

The tests performed in presence of major fouling species like *Amphora* sp., *Ulvarigida*, *Polysiphonia sphaerocarpa*, *Bugula neritina* and *Amphibalanus amphitrite* showed that all the tested fouling organisms were inhibited by the samples with only nanoscale roughness, while nano- and micro-scale architectures seemed to be less effective with more fouling settlement observed.

In order to study local changes in electron density contrast due to partial or complete wetting of a rough interface, small angle X-ray scattering technique evidenced the presence of air pockets or nanobubbles at the interface of the immersed superhydrophobic coating. (Fig.2)

One of the present authors in [Krasowska,2011] has also shown the influence of the immersion angle of a superhydrophobic surface in the wetting properties of a surfactant solution and the bubble attachment.

Since superhydrophobicity mainly benefits of the air entrapped in the grooves of a solid surface or coating, the presence of very small volumes of air at nanoscopic scale (nanobubbles) has been matter of a wide range of interpretations and observations.

Despite the existence of nanobubbles at hydrophobic surfaces is still under a debate, is worth to cite the interesting work [Craig, 2012] where the authors try to make order among controversial results but also exploring applications for nanobubbles.

Theoretically such bubbles should dissolve under their own internal pressure within a short time, but, in comparison to a relevant number of results inconsistent with the presence of nanobubbles, even working with highly surface sensitive techniques, Atomic Force Microscopy (AFM) has been successfully used to describe the peculiar evidence and the unusual properties and shapes of nanobubbles.(Fig.3)

Working in tapping mode in water, AFM directly imaged the phenomenon of nanobubbles. Shortly, even if this technique has become a routine in imaging biological soft samples in liquid, studying nanobubbles in tapping is quite hard being influenced by the imaging conditions [Zhang, 2006], in spite of their morphology have largely benefit. The tapping mode is to be preferred to AFM contact mode, being the latter more suitable for hard surfaces and nanobubbles too soft bodies to be revealed.

SELF HEALING MATERIALS

The ability for a surface to repair itself (self healing) is mimicked after naturally occurring or biological systems. Natural healing processes have inspired the recent research in self healing coating and this approach is generally termed biomimetic or bioinspired, even if non-living systems have also shown similar mechanisms.

Natural systems use protective coatings over various substrates: skin, cell membranes, tree bark, plants wax, etc. protect the underlying substrates.

Synthetic coatings have been similarly developed for the protection of the substrates on which they are deposited.

Natural systems and synthetic or artificial coatings are different mainly in the way they repair themselves after damage.

Skin naturally reproduces itself holding to a basically identical surface, while in plants we find a continuous renovation of leaves surfaces by wax crystals preventing growth of contaminant agents, like fungi, in water or humid environment.

In non-living system we can find a similar mechanism when the thin oxide layer present on the surface of aluminum or other metals undergoes to a self repair after a scratch to protect the bulk metal.

The main concept behind the design of self healing coatings is the incorporation in a bulk matrix of an healing agent, usually in capsules which can open and release the content upon damage of the coating. (Fig.4)

Despite the efficiency of these methods in repairing a wide selection of possible damages, the resulting surface formed over the scratch shows different, if not less, protective properties in comparison with the original undamaged surface.

Originally, encapsulated self healing materials have been introduced in [White, 2001]

Once a damage event occurs in these coatings the cut or the impact produce the rupture of the capsules and the encapsulated monomer, in this case dicyclopentadiene (DCPD), flows by capillarity into the crack polymerizing by effect of the catalyst in the resin of the matrix.

Since the initial publication, due to its potential, the topic has grown in many different directions [Bryan, 2009; Blaiszik, 2010; Hager, 2010]

Self healing materials can be finally foreseen as a suitable solution not only to enlarge the longlasting durability of the protective coatings in marine environment during navigation, but also could be efficiently tested in circulating plant waters provided a careful control of safety and technological issues related to a long time use.

BOAT AND SHIP HULLS

The phenomenon by which every surface immersed in seawater undergoes colonization by biological organisms regards, of course, boat and ship hulls. Other surfaces in service for example in open sea oil platforms will not be taken under consideration in this work.

The most important impact connected to biofouling phenomena is the enhancement of the fuel consumption due to the increased frictional drag, with respect to other costs linked to hull maintenance such as cleaning and painting, with enormous annual economical impacts (about 1 billion USD [Callow, 2002]). Hence, as stated by the some authors [Schultz, 2011], it is clear how even exiguous improvements in the fouling condition of a hull allows to afford money that can be used in development, implementation and research of fouling control technologies.

Since the large scale employment of self-polishing copolymers loaded with tributyl tin (TBT) as the biocide in early seventies [Evans 1999], the problem of fouling growing on hulls has been faced with solutions that deeply evolved in recent years as a consequence of the ban of these products by the International Maritime Organization (IMO) in 2008 [Molino, 2009]. The success of TBT ablative compounds was based on the non selective biocidal effect of impairing larval settlement [Terlizzi, 2001], the very high non-targeted toxicity [Goldberg, 1986] and on the effects lasting as long as the required entire docking serving period [Townsin, 2003]. In turn, coniugating these prerogatives with the bioaccumulation and the residential time of days (even longer if absorption to particles and sediments is considered [Stang 1992.]), it is easy to figure out why heavy environmental costs were largely experienced all around the world [Evans 1999] and the decision of a TBT ban arrived.

An environmentally acceptable alternative to biocide-based antifoulants is represented by non-toxic approaches, such as foul-release and biomimetic strategies [Chambers, 2006]. The principle of foul-release coatings is based on weak attachment that organisms involve with surface due to the low surface energy, allowing easy removal by shear as the hull moves through the water at speeds between 10-20 kts.

In recent years, the rapid improvement in technologies aiming to make the surfaces highly water repellant rendering them superhydrophobic, allowed investigations in naval applications in order to investigate anti-friction and foul-control properties of these coatings.

In order to consider a superhydrophobic surface for fouling control purposes, it is required that inhibition of colonization processes has to be exerted from the stages of fouling formation where the friction drag effects starts to be present. In addition, in order to encounter large-scale applications needs (as coming from surfaces of ship hulls), the production, storage, application, and maintenance technology must be economic and green.

TIME SCALE OF BIOFILM FORMATION

In general (Fig.5), the biofouling begins with the inevitable formation of a molecular 'conditioning' film consisting of glycoproteins, humic acids, proteins, aromatic amino acids, carbohydrates, uronic acids and/or unspecified macromolecules [Jain, 2009]. The adsorption of dissolved organic material on to the clean surface is very fast and occurs few minutes after immersion in seawater. The successive stages bring to the formation of a film, mainly composed by sessile bacteria, microalgae including diatoms, microscopic fungi, heterotrophic flagellates and sessile ciliates (heterotrophic protists) [Salta, 2013], with bacteria and diatoms often being the dominant taxa. This first assemblage of attached cells, sometimes referred to as 'microfouling' or 'slime', is called biofilm

[Callow 2002]. Successive phases involve the growth of diatoms, other algae, and invertebrate larvae [Cooksey, 1995].

From a biological point of view this layer is of crucial importance since allows the colonization of superior species. From an ingegneristic point of view, the biofilm is important as well, since it exerts a significant detrimental effect upon ship navigation performances. Although the slime formation is a phenomenon dependent on several variables and it is impossible to predict the tendency of the slime characteristics developing on a certain hull surface [Townsin, 2003], as reviewed by the cited author, numerous published data coming from the field ascertain efficiency losses compressed between 5 to 25 % due to friction drag induced by the slime formation [Watanabe 1969, Conn 1953]. The importance of resistance provided just at early stages of biofouling formation is confirmed elsewhere [Holma, 2004].

The most evident conclusion, as stated by some authors [Schultz, 2000], is that biofilms should be considered when addressing the need for hull cleaning, due to the significant increase of the skin friction drag on marine vehicles.

In this sence, two questions are crucial when superhydrophobic surfaces are devoted to ship hulls applications. The first, concerns the friction reduction *per se*, the second, concerns the interaction between superhydrophobic surfaces and biofouling from the early stages of its formation.

FRICITION AND DRAG REDUCTION

The friction drag reduction of clean (not yet fouled) superhydrophobic surfaces was reviewed by Zhang et al. [Zhang, 2008], who asserted that the generation of a thin layer of air at the solid/liquid interface establishes an air/water new boundary condition. In recent years, some authors [Su, 2010] experimentally verified a faster movement of a superhydrophobic ball on the water surface due to reduction of skin friction depending on the increased area of the solid/atmosphere interface. Consistently, Dong et al. [Dong, 2013], attributed the observed reduction of the friction drag on a model ship with a superhydrophobic coating to the replacement of the liquid/solid interface with a liquid/bubble/solid interface, less resistant than the liquid/solid one. The authors recalled on the 'plastron effect', a peculiar feature of many insects and spiders, which are able to survive underwater due to a thin air layer trapped along their exteriors, acting as a respiratory bubble or 'plastron', wherein the diffusion of dissolved oxygen from the water takes place [Flynn, 2008].

The implications on naval industry of how the superhydrophobic surfaces can reduce the friction drag, can be easily figured out considering the economical premises provided at the beginning of the paragraph. As a consequence, the necessity of the preservation of the surface superhydrophobicity has to be evaluated from the first stages of the biofouling formation processes, i.e. the adsorption of

molecules constituting the conditioning film. As seen, the adsorption of these molecules is rapid, occurring in within minutes-hours, and is crucial, since is functional in driving further stages of biocolonization where superior organisms are involved.

ADSORPTION PHENOMENA IN SEAWATER

At this level of the biofouling formation, the importance of adsorbing substances like surfactants, proteins and EPS (extracellular polymeric substances) is in general related to the adhering strategies of pioneer organisms (mainly bacteria and diatoms) that initiate to colonize the surfaces and to build up the slime. In particular, initial adhesion processes in biofilms are related to the protein component of the extracellular polymeric substance, which are composed of polysaccharides, proteins and nucleic acids [Flemming 2001]. More in general, the complexity of adhesion strategies and modalities of marine organisms, mainly based on the action of adhesive polymers, are extensively and deeply treated in [Smith 2006], covering the biofouling temporal-dimensional gradient from bacteria and diatoms to barnacles and mussels. Superior organisms use adhesive proteins as well [Stewart 2011].

Hence, when it is looked at highly-super hydrophobic surfaces as a non-toxic biofouling control strategy, it has to be considered how do these surfaces behave when they interact with biopolymers and/or other macromolecules at the first stage of the biofilm formation. The necessity to consider biofouling processes in marine environments starting from the adsorption of biopolymers which are functional to bioadhesion and allow, *de facto*, further colonizations, is clearly manifested by [Vladkova 2008], and is introduced by [Gunari, 2011] and [Koc 2008], who asserted that ‘Protein adsorption is the first stage in biological contamination of surfaces [..]. Surfaces that hinder or obstruct this early adsorption process would reduce cell growth’ (referred to marine biofouling processes too).

In literature, the relationship between highly-super hydrophobic surfaces and molecules adsorbing during the very initial stages of biocolonization (conditioning film stage) in seawater is relatively less explored with respect to the relationship of these surfaces and bacterial slimes.

Nevertheless, in fields like bioengineering and biotechnology, where the adsorption of proteins to surfaces is of interest and the aim in several applications is to control/inhibit the protein adsorption, interesting arguments for marine applications can provide some inspiration points [Ospinal-Jiménez, 2012].

Ostuni et al. [Ostuni 2003] found that proteins adsorbing on hydrophobic islands lose their conformation, and this process is more intense as the density of the hydrophobic groups is higher. Other authors [Roach 2006] showed that different sized adsorbing proteins (bovine serum albumin,

□14 × 4 nm, vs. fibrinogen, 46 × 4 nm) exhibited a different degree of denaturation depending on surface wettability and topography (Fig.6). Moreover, superhydrophobic surfaces can determine a reduction in the rate of protein adsorption due to the reduction in solid surface area at the liquid interface if the Cassie–Baxter bridging case is considered [Sun 2005; Lourenc 2012], and, under flow shear similar to that encountered in microfluidic devices (1-10 μl min⁻¹), superhydrophobic surfaces promoted an easy removal of proteins adsorbed under static conditions [Koc 2008]. Similarly, as recently observed by Anselme et al. [Anselme, 2010], protein adsorption is influenced by nanotopography, which, in turn, influences cellular and bacterial responses. The cited author concluded that ‘future research in the field should concentrate on the conformation of proteins on nanomaterials, since it is the protein conformation that cells or bacteria react to’.

Hence, it can be argued that the control of superhydrophobic surfaces in the adhering mechanisms at the first stage of the marine biofouling evolution can be exerted not directly preventing the adsorption of biopolymers, rather, likely, (i) reducing the available adsorption sites due to the air trapment in the nano-textured surface, (ii) inducing conformational changes in adsorbed adhesive proteins, (iii) driving selective adsorption/denaturation processes, (iv) promoting the detachment of adsorbed proteins in non static conditions.

As consequence, the composition/conformation of the resulting protein layer and the conformation and orientation of the proteins may drive cellular attachment/adhesion stages [Elbert 1996].

Looking at the seawater, questions can be focused on factors that can limit or modify the efficiency of these controlling mechanisms. As suggested by [Hook, 1998], how the adsorbing processes on superhydrophobic surfaces can be influenced by pH and ionic strength as in seawater? Some authors [Hwanga 2012] found low adhesion at high ionic strength for two different bacterial strains. In addition, to which extent non-proteic adsorbing molecules constituting the conditioning film can interfere in the protein adsorption/denaturation events occurring on superhydrophobic surfaces, resulting, in turn, in changes of bacterial adhesion?

The present authors have recently studied the effect of surface active molecules on the interfacial properties of seawater [Guzmán, 2014].

The importance of the adsorption processes of proteins and others molecules at the stage of the conditioning film is underlined by Genzer et. al [Genzer, 2006] about the modification of the surface energetics. The cited author recalled on Fletcher & Pringle’s work [Fletcher, 1985], where it is evidenced the role of any dissolved macromolecules adsorbing on surfaces and influencing the surface tension of the liquid and hence the thermodynamics of adhesion resulting, once more, in the statement pronounced by [Callow 1994], that ‘any discussion of the influence of surface energy on

bioadhesion must recognize that the clean surface will have been modified to a greater or lesser extent before adhesive events take place'.

Some authors [Bakker 2004] touched these items determining the changes in surface properties of experimental polyurethane antifouling coatings after immersion in natural seawater and relating these changes to the deposition of three marine bacterial strains. The cited authors found that the conditioning film formation brought changes in hydrophobicity (reducing CA on hydrophobic coatings and enhancing CA on the hydrophilic ones), roughness (that resulted to be enhanced) and chemistry (with enhanced amount of nitrogen on the surface due to the adsorption of proteinaceous material) with subsequent changes in the marine bacteria adhesion. They concluded the maintainance of foul control properties after exposure to natural waters requires that conditioning film formation should be a first target in the development of antifouling coatings. A confirmation of this standpoint is indirectly provided by Stallard et. al, [Stallard, 2012], who witnessed the lowest protein adhesion on superhydrophobic coatings with the lowest bacterial attachment.

Hence, it is clear that the highly-super hydrophobic as non-toxic foul-control approach must necessarily face the first stage of the bioadhesion evolution, i.e. the adsorption of biopolymers constituting the conditioning film.

At this stage, investigations are needed in order to verify 1) to which extent the adsorption processes can modify the superhydrophobic surface parameters (CA, CAH, surface tension, micro-nano topography,...), i.e. properties providing both friction reduction and inhibition of the colonizing organisms, 2) as suggested by [Anselme, 2010], who affirmed that future research might investigate conformation of proteins on nanomaterials (since it is the protein conformation that cells or bacteria react to), how to exploit the superhydrophobic capacity in determining adsorption inhibition, denaturation, and eventual detachment of foregoing/adhesive biopolymers in seawater at the initial stages of adhesion (protein-EPS level), making the surface something different and/or difficult to be recognized by colonizing organisms.

Moreover, unless superhydrophobic surface is able to transformate the conditioning film modifying (hopefully inhibiting or slowing) successive settlement processes, another important aspect regards the time duration of these modifications, until the biologic pressure is likely expected to recover the surface to an equilibrated state suitable for successive colonizations. This consideration is suggested by Zhang et al. [Zhang, 2005] who investigated fouling in relation to nano-rough surface and superhydrophobicity. The cited author found that the fouling resistance in the field decreased over a 2-month period. The loss of superhydrophobicity, as the determining cause, was proposed to be induced by air dissolving in water over long periods of submersion depending on 1) the loss of air from the water-solid interface due to the deterioration of pores, 2) the modification of

chemical and physical structures of the surface due to the formation of a conditioning layer of macromolecules.

Following the time evolution of the biofouling colonization and moving from macromolecules adsorption taking place within hours towards the adhesion of the most elementary organisms (e.g. bacteria and diatoms, attaching in hours-days), literature provides studies dealing with the interaction of superhydrophobic surfaces and bacteria. Considering that the microbial slime is decisive in driving the subsequent formation of biofouling on surfaces, and that it exerts an important effect *per se* on the friction drag on ship hulls. The question whether 'superhydrophobic surfaces can reduce bioadhesion', as it was formulated with these words by [Genzer, 2006] in an 8 years ago review, is crucial as well.

The bacterial adhesion on highly water repellent surfaces was reviewed mainly depending on the surface energy, the hydrophobicity and on the surface topography.

About surface energy, as reviewed by [Genzer 2006], several authors showed a minimum of bacterial adhesion in a 20-30 mJm⁻² range (consistently with pioneering Baier's findings in the late 1960s), which was indicated by [Callow 1994] as the requirement to be satisfied by coatings to behave as foul-release surfaces. The same author mentioned tests on silicone coatings performed between 80° and 90° [Meyer, 1988], emphasizing how they underwent a slower rate of fouling accumulation with a better tendency to be cleaned easily. Thereafter, the promising and encouraging results of the non-toxic low-energy approach was stated in successive years [Tsibouklis, 1999] opening the doors to the foul-release technology, about which a recent and comprehensive review was published [Lejars, 2012]. The general observation that microorganisms attach more rapidly to hydrophobic nonpolar surfaces than to hydrophilic materials belongs to [Mazumdera, 2010], who, in addition, ascertained a decrease in the hydrophobicity after the bacterial attachment. These aspects are of particular importance when the attachment phenomena are considered on superhydrophobic surfaces, which are less suitable to attachment than hydrophobic ones, with a non linear dependence of attachment phenomena on the CA. Hence, once a superhydrophobic surface is immersed in seawater, adsorption of macromolecules and biopolymers at the stage of the conditioning film formation can lower the contact angle to an extent potentially more suitable for the next coming organisms. Nevertheless, as previously discussed, the effective attachment results could be influenced by the peculiar configuration obtained by the conditioning film in dependence to the adsorption and interaction processes at the superhydrophobic surface.

SUPERHYDROPHOBIC SURFACES AND FOULING CONTROL

Fouling control properties of superhydrophobic surfaces can be obtained by nano-micro functionalized surfaces trapping air with a deterrence and prevention effect over biocolonization processes. [Scardino, 2009; Myan, 2013]. Nevertheless, topographic surface structures can exert effects over settlement processes, even in absence of trapped air.

The ripple structure featuring a distance between two ripples of approximately 1-2 on the periostracum of blue mussels, reduces the settlement of barnacle larvae, in turn, when the microtopography is eroded, these repellent effects disappear [Scardino, 2003]. For surface topographies in the micro-scale (< 500 μm) domain, a selective action in inhibition was observed in function of the size of the superficial protrusions, [Bers, 2004]. In particular, in the micro-scale surface design, significant results were obtained targeting on alga *Ulva*. Schumacher et al. [Schumacher, 2007] evidenced how surfaces patterned with micrometric size features reduced the settlement of *Ulva* spores (Fig.7).

Nevertheless, comparison among features with the same width and spacing (2 μm) topographies, the best inhibiting settlement result was associated with the Sharklet AFTM design, constraining the inhibiting effect to depend on the feature geometry and tortuosity. All cited investigations showed clearly that inhibiting effects are specific to certain settling organisms, and that roughness and spacing in designing topographic surfaces must be considered as well. Some authors showed that at short times of exposition (hours), [Crick, 2011], the main attachment areas on the superhydrophobic films were the tops of the surface protrusions, i.e. the available fraction of area where the contact between aqueous suspension and surface protrusions actually exists, excluding surface areas where air is trapped. The prevention of bacterial attachment by reduced contact area on superhydrophobic surface due to air trapped was demonstrated by Truong et al. [Truong, 2012], who observed that the progressive wettability of the in water resting surface was counterbalanced by the attachment advance. Bers et al. [Bers, 2004] ascertained that the time duration of correlated effects decreased, consistently with other authors' findings [Andersson 1999; Chung, 2007].

Hence, micro-nano textures surfaces are able to play inhibiting effects per se, in case air is trapped (when the surface is immersed, or the air is not yet dissolved) even more repelling effects are still conserved as soon as highly to super-hydrophobicity is still preserved. Of course, the integrity of the surface topography in relation to abrading phenomena still remains crucial for the time duration of functionalized surfaces in service in a long time scale (years, as for ship hulls).

A recent publication provides clear insights into this argument [Vuckoa, 2014], evaluating the settlement prevention and release enhancement of marine fouling organisms of a series of $\square\text{m}$ textured and non-textured polydimethylsiloxane surfaces. The cited authors, performing laboratory

and field tests, showed that in the field textured surfaces lost their deterrent effect after six months and showed high rates of settlement regardless of textures. Analogously, time duration regards long-lasting performances of inhibiting effects of superhydrophobic surfaces as well.

A step towards the prolongment of foul-control properties was recently made synthesising superhydrophobic films containing dispersed silver nanoparticles [Liu, 2012], where the bacterial adhesion control, after the deterioration of topographic texturing providing superhydrophobicity (observed in one week), was prolonged by the nano sized Ag particles dispersed in the polymeric matrix and released in the solution. The strenghtening of superhydrophobic coatings with nano sized Ag was investigated even by [Heinonen, 2013]. For ship hulls applications, drawbacks of these solutions are the Ag biocidal effect (resembling, in principle, TBT ablative paints), economical limits for large-scale applications, and, the needs laying in a temporal order of years (not weeks-months).

The time maintenance of foul control properties of an engineered surface at the development stage of the bacterial-diatomeic slime has to be evaluated including the role of detachment forces as a variable determinant not only for the removal of microfouling organisms from surfaces, but also as a variable able to drive particular structures and composition of the microfouling communities when exposed to shear stresses.

This aspect is suggested by some authors [Liu, 2001], who reviewed how relatively higher detachment forces can induce significant modifications on the biofilm evolution since its early formation stages, in particular determining a more compact and denser biofilm, influencing the structure, mass transfer, production of exopolysaccharides, metabolic and genetic properties. Analogous findings were highlighted by other authors [Woods 1986; Finlaya, 2013]. The first evidenced how the surface of ships where the flow regime changed from laminar to turbulent experienced a change in the floristic composition of the diatom population, the second evidenced the correlation between biofilm attachment processes and shear stress appliance during culture period.

Therefore, it is important to consider the result of attachment-detachment equilibria of colonizing diatoms and bacteria on superhydrophobic surfaces when periods of quasi-static flow regimes (harbour rests) are opposed to non-static navigation phases.

Some investigations showed how it is possible to combine superhydrophobicity, low surface energy and micro-nano topography. Superhydrophobic surface resulting by the combination of micro and nanostructured features from silica colloids and a low surface energy fluorinated silane xerogel reduced the adhesion of highly pathogenic bacteria by ≈ 2 orders of magnitude versus controls [Privett, 2011]. Nano-structured silicon oxide type coatings deposited on glass slides from a

hexamethylsiloxane precursor (23–46 mJ m⁻¹ surface energy, 42-94° contact angle) exhibited anti-fouling (i.e. reduced settlement) and fouling-release (i.e. release of attached organisms under defined shear stress) performances when tested against marine algae and some bacteria [Akesso, 2009]. Other authors [Vuckoa, 2014].

Firstly, since the surfaces are wide, production, storage, application methods of superhydrophobic treatments and their maintenance procedures have to encounter economic and 'green' criteria. In addition, once a new superhydrophobic surface is immersed in seawater, modifications of surface properties are expected to occur since the first stage of the biofouling processes, i.e. during the early (minutes-hours) development phases of a conditioning film with the adsorption of macromolecules and biopolymers.

Finally, looking at superhydrophobic technology as a surface finishing method aiming to inhibit the biofouling formation on ships hull, questions deserving wider investigations can be resumed as follows: how do these modifications interfere (if any) with settlement/adhesion processes? In case of surface regeneration, which is its reversibility degree? Is the biological pressure of colonizing organisms in a real seawater environment expected to fade out the superhydrophobic properties?

OTHER APPLICATIONS

Another important field where biofouling and corrosion phenomena are of relevance is the heat-exchange (coolant) and desalination technology, where the operative conditions that protective coatings might face are particularly aggressive.

These aspects concern the fact that the fluids circulating in plants and finally rejected have particular characteristics. In general, for desalination plants, components present in waste effluents consist in corrosion products, antiscaling, antifouling, antifoaming, anticorrosion additives, halogenated organic compounds formed after chlorine addition, oxygen scavengers (sodium sulfite), oxygen deficiency, acid, heat, salt concentration [Höpner 1997].

In case of protective coatings (e.g. superhydrophobic) effective in controlling biofouling and corrosion phenomena, traditional antifouling and anticorrosion treatments could be limited or avoided. Differently, there are several modifications of circulating fluids that a protective coating has to face in any case. These regard antiscaling compounds (acids or advanced scale-inhibiting reagents), added to the feedwater of both thermal or reverse osmosis (RO) plants [Likhachev, 2013] to prevent calcium carbonate scale formation on the heat transfer surfaces. Generally, antiscalants are referred to polymeric substances with different chemical structures, in particular polyphosphates, phosphonates, polymaleic acids and polyacrylic acids [Lattemann, 2008; Gusmano,

2005]. Antifoaming additives are referred to non-ionic surfactants [Imama, 2000]. Substances like polyglycol monoalkyl ethers were tested as well [Auerbach, 1981].

In addition, salinity of the concentrate wastewater is generally enhanced (up to 65-85 mg L⁻¹ for RO plants and about 50 mg L⁻¹ for thermal MSF), while about temperature, in the discharges of thermal plants, which are characterized by higher values than that at the intake, temperatures can reach enhancements of 5 °C to 15°C above ambient [Lattemann 2008].

As anticipated before, treatments for the control of biofouling and corrosion phenomena could be saved (totally or partly) in presence of an effective superhydrophobic coating. These consist in biocides, mainly chlorine compounds [Lattemann, 2008] (added or generated in situ [Abdul-Wahab, 2009]), and corrosion inhibitors (e.g. benzotriazole derivatives [S. Lattemann, 2008]).

The biofouling control properties of superhydrophobic coatings in open waters on ship hulls, as seen in the previous paragraph, is far from being a simple task to be investigated and explored, at the present. Analogous criticisms can be figured out in applications where seawater is made to circulate in plants. Although speeds of seawater circulating in heat exchange-cooling circuits of power and desalination plants (1-5 m s⁻¹ [Nebot, 2007; Larché, 2011; Trueba, 2013]) can stimulate detachment processes from the superhydrophobic surfaces, the flux itself can exert abrading phenomena on coatings due to the content of suspended particles, accelerating the deterioration of its protective features. In addition other degrading processes may result from the permanent contact of the coatings with relatively warm, saline and polluted fluids (as resumed before).

Hence, physical-chemical and mechanical resistances of these coatings are required.

AGING AND DURABILITY UNDER SEVERE CONDITIONS

While the chemical and mechanical resistance of a SH coating is still an issue to be overcome at lab level, there is a lack in literature of works directly devoted to durability in sea waters. The present authors performed two campaigns in summer 2013 and 2014 with the aim to correlate the performance of a SH mixed organic-inorganic coating [Ferrari, 2006] to various parameters in a controlled real sea environment [Ferrari, 2014].

Some authors [Zhu, 2011] investigated the mechanical durability of a superhydrophobic metal/polymer composite surface produced by a hot pressing approach followed by Ag deposition and surface fluorination. The superhydrophobic surface was dragged on a 1500 mesh sandpaper with a 10 kPa pressure in one direction (3 cm s⁻¹ speed, 30 cm abrasion length). After being scratched repeatedly, high water CA (more than 150°) due to Ag dendritic microstructures rough surface textures were still observed. The authors noted that the abraded part represented more less than 10% of the entire superhydrophobic coating (nearly 15 μm against 180 μm), and, more

interestingly in the light of self-repairing properties in an abrading environment, the freshly exposed surface originated by abrasion preserved its superhydrophobic nature with CA larger than 150°.

Still in the direction of industrial applications, some authors [Rao, 2011], performed chemical aging tests, demonstrating that the superhydrophobic nature of anticorrosion coatings developed with a sol-gel deposition on copper was maintained after soaking of the film for 100 h in 50% of HCl solution. Xu et al. [Xu, 2011], investigating the anticorrosion properties of a superhydrophobic magnesium alloy, explored its durability highlighting effects of the exposure time to air, pH values, and immersion time in the 3.5 wt % NaCl aqueous solution. Liu et al. [Liu, 2013], evidencing anticorrosion performances of bayerite needles fabricated by etching of the Al foil exhibiting a micro-nano surface roughness, revealed a good resistance against acid and alkali solutions of the so obtained superhydrophobic surfaces, attributing it to the barrier effect of “air pockets” between the Al solid substrate and the solutions. Good mechanical resistance is mentioned as well.

A recent work by Wang et al. [Wang, 2011] provided a demonstration of this aspect. In particular, the cited author showed how deaeration with ethanol of superhydrophobic interface obtained on Zn determined 1) the open circuit potential (OCP) of superhydrophobic not deaerated sample to be nobler by nearly 400 mV with respect to the OCP of both bare and deaerated superhydrophobic samples, 2) the value of the interfacial capacitance of superhydrophobic sample to be very lower with respect to deaerated superhydrophobic sample. The cited authors concluded that the air trapped in the film can improve the anti-corrosion effect behaving as a dielectric for a parallel plate capacitor limiting electron transfer between the electrolyte and the substrate (Fig.8).

SUPERHYDROPHOBIC SURFACES AND CORROSION ASPECTS

More in general, corrosion protection performances of superhydrophobic coatings (preferentially in NaCl 3.5% solution) is a literature topic. The slowing-down of corrosion processes performed by a superhydrophobic interface is generally evidenced with lower anodic currents registered during potentiodynamic scans and larger values of the resistance charge transfer obtained during electrochemical impedance spectroscopy tests [Liu, 2007; Zhang, 2008; He, 2009; Yin, 2011; Zhao, 2014]. In many cases, these results are attributed to the presence of air trapped in the micro-nano structures of the superhydrophobic coating/finishing [Liu, 2007; Wang, 2012, Liu, 2013].

Still in anticorrosion properties of superhydrophobic surfaces, Yin et al. [Yin, 2008] investigated the properties of myristic acid, chemically adsorbed onto anodized aluminum surface. Other authors [Zhang, 2008] investigated superhydrophobic coatings obtained by nAl-LDH-laurate film, evidencing the duration of these performances over weeks time-scale.

Hence, is clear that for industrial applications regarding the use of superhydrophobic coatings, once

ascertained the efficiency of anticorrosion properties, and once a full comprehension of foul control phenomena are to be delucidated, in any case durability requirements depending on resistance against aggressiveness of circulating fluids are needed. As seen, from the literature is demonstrating that this could be a possible direction where future investigations efforts and energies can be addressed to. [Liu, 2010]

CONCLUSIONS

The possibility of water repulsion on surfaces is a very attractive solution which finds applications in many fields. One of these is the inhibition of biofouling formation on surfaces where the interaction of seawater occurs (e.g. ship hulls, desalination plants, etc.). This review summarizes critical aspects related to the production of superhydrophobic coatings and their use in seawater applications, where the possibility of a non-toxic approach has to face important aspects still representing open challenges.

For ship hull surfaces, where the frictional drag due to the biofouling formation implies the heaviest bio-induced economical impact, in literature are present works dealing with the capability of superhydrophobic coatings in inhibiting the biofouling formation mainly at the stage of bacterial slimes, in modelled solutions, within a days-to-month time scale. In comparison, the effects of macromolecules (adsorbing on surfaces within minutes-hours) on the superhydrophobic properties of coatings in model solutions as well as in natural seawater are less studied.

More in general, for applications in open seawater (e.g. ship hulls) or seawater solutions circulating in plants (e.g. desalination, power plants), the main challenge is to guarantee the durability of the superhydrophobic properties of coatings consistently with maintenance interventions periods (months-years time scale). In particular, for seawaters circulating in plants, this aim is complicated by the chemical-physical aggressiveness of circulating seawater solutions

ACKNOWLEDGEMENTS

The authors acknowledge RITMARE Flagship Project SP 1, WP 2, WP 5 Call IENI/004/2013/GE for the financial support

FIGURE CAPTIONS

Fig. 1 Scanning profilometer (SENSOFAR) image of a mixed organic-inorganic coating with superhydrophobic properties (Two scale roughness on the order of tens and hundreds of nanometers)

Fig.2 Comparison of fouling attachment on the SHCs (&) and glass (⊠). (a) SHC 1; (b) SHC 2; (c) SHC 3. Data are means, n ¼ 5. Treatments with an asterisk have a significantly different number of attached organisms than expected compared to glass using a Chi-square test (w).

Fig.3 AFM tapping mode images of nanobubbles on HOPG in water. Image size 10 μm × 10 μm. In the lower image it can be seen that the imaging process has led to the removal of bubbles in a 4 μm × 4 μm area.

Fig.4 Self-healing with the help of microcapsules.

Fig. 5 Schematic of the biofouling process. A clean, unprotected surface becomes fouled with organic molecules within seconds of ocean submersion. These macromolecules are on the nanometer size scale. Microorganisms such as bacteria and diatoms attach within minutes and form a biofilm within hours. Macrofoulers such as spores of algae and larvae of tube worms and barnacles begin to attach within hours. A mature fouling community forms over a time frame ranging from days to months.

Fig.6 Saturation curve for BSA adsorbing onto hydrophobic substrates with radii of 82 nm. Error bars show standard deviation.

Fig. 7 SEM images of engineered topographies on a PDMS surface. (A) 2 mm ribs of lengths 4, 8, 12, and 16 mm combined to create the Sharklet AFTM; (B) 10 mm equilateral triangles combined with 2 mm diameter circular pillars; (C) hexagonally packed 2 mm diameter circular pillars; (D) 2 mm wide ridges separated by 2 mm wide channels

Fig.8 Interface model for the superhydrophobic film in 3.5% NaCl solution (the shaded part represents the metal complex film).

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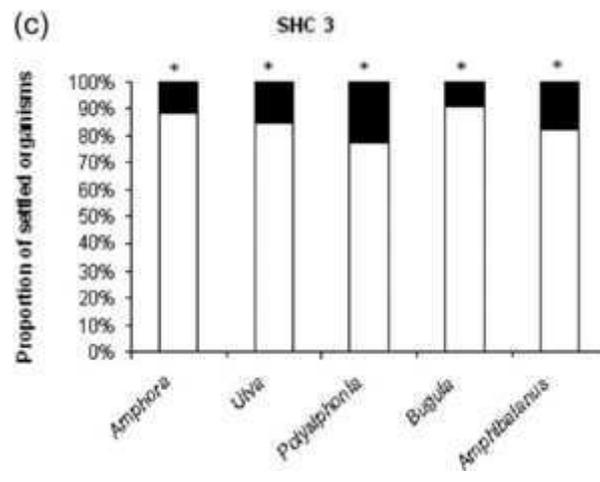
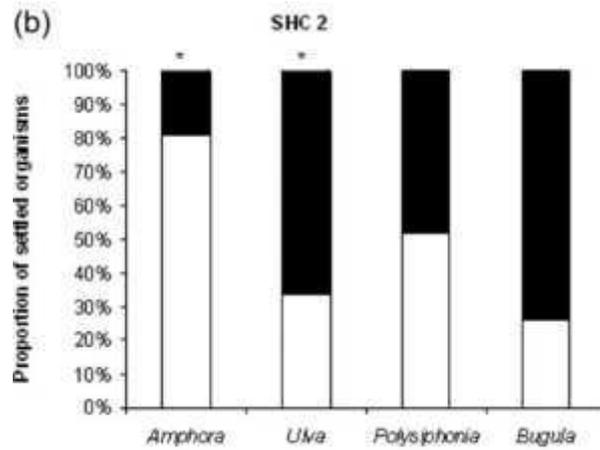
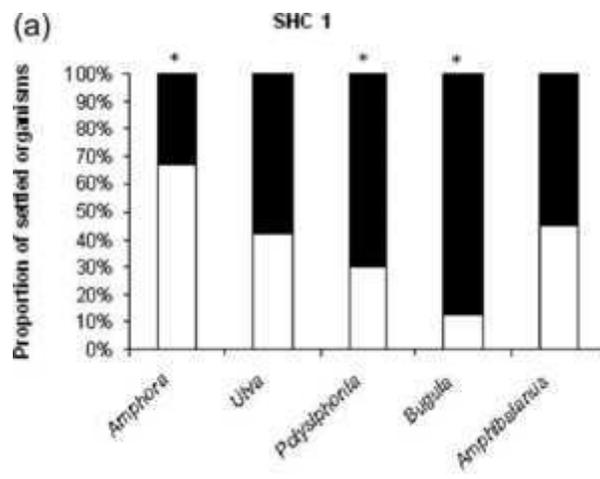
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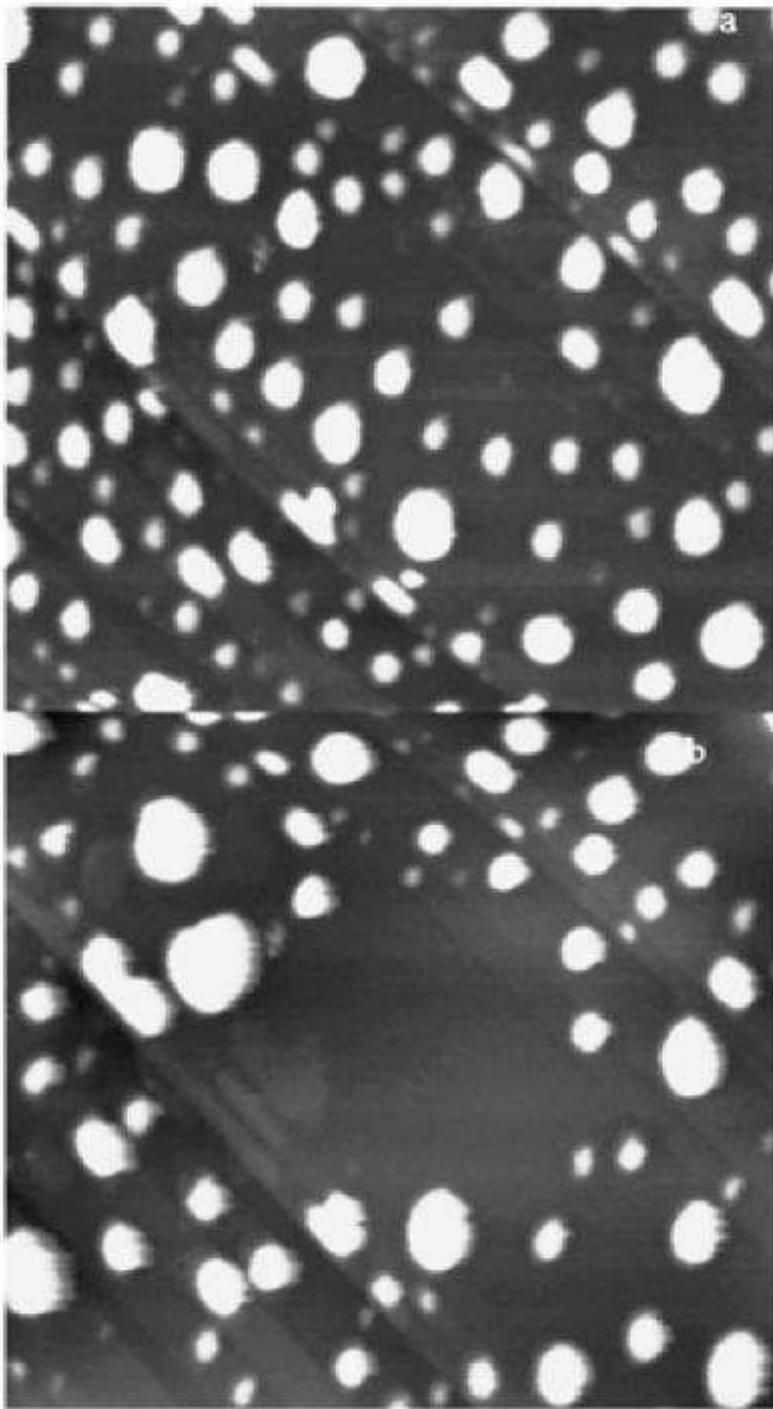
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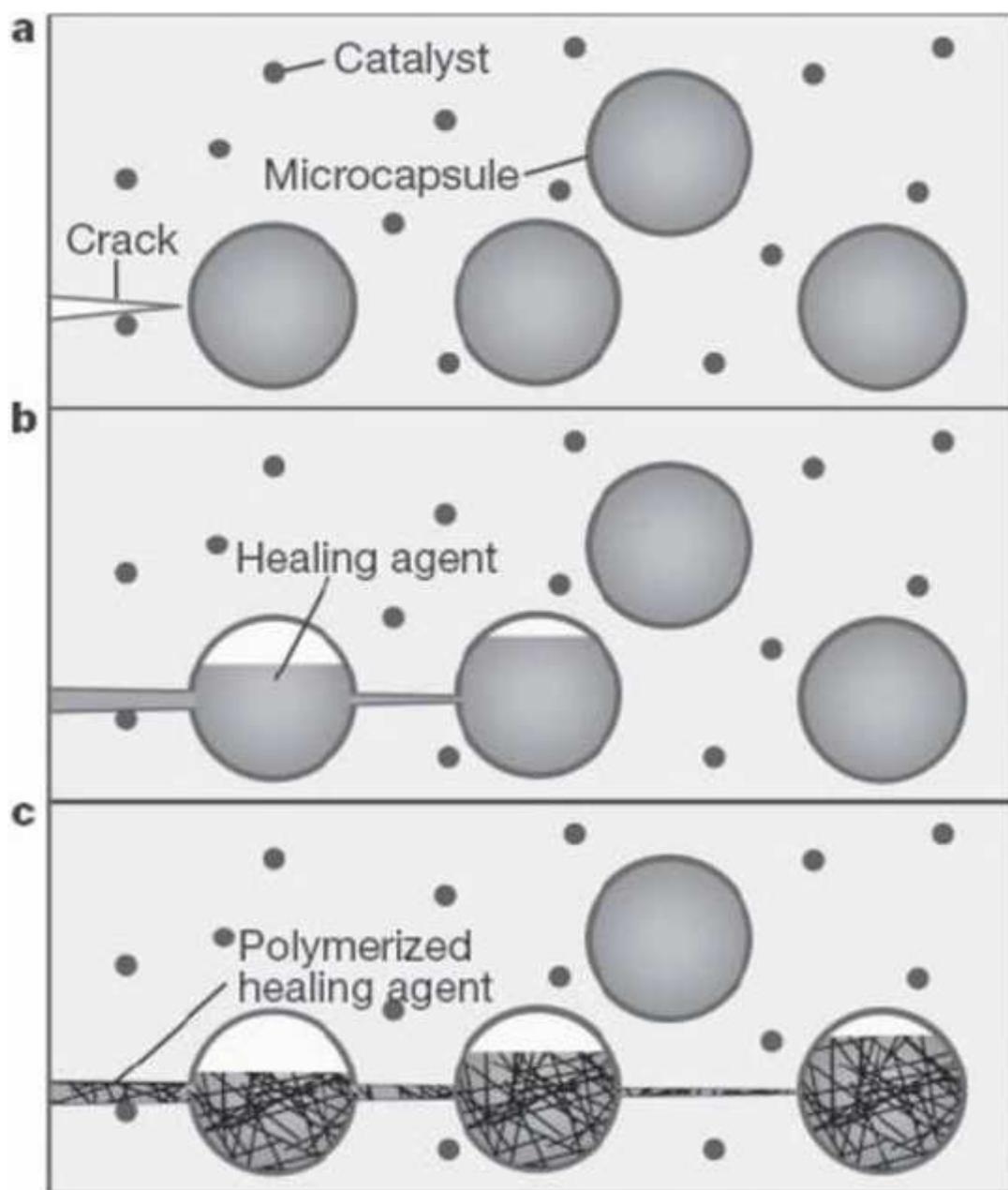
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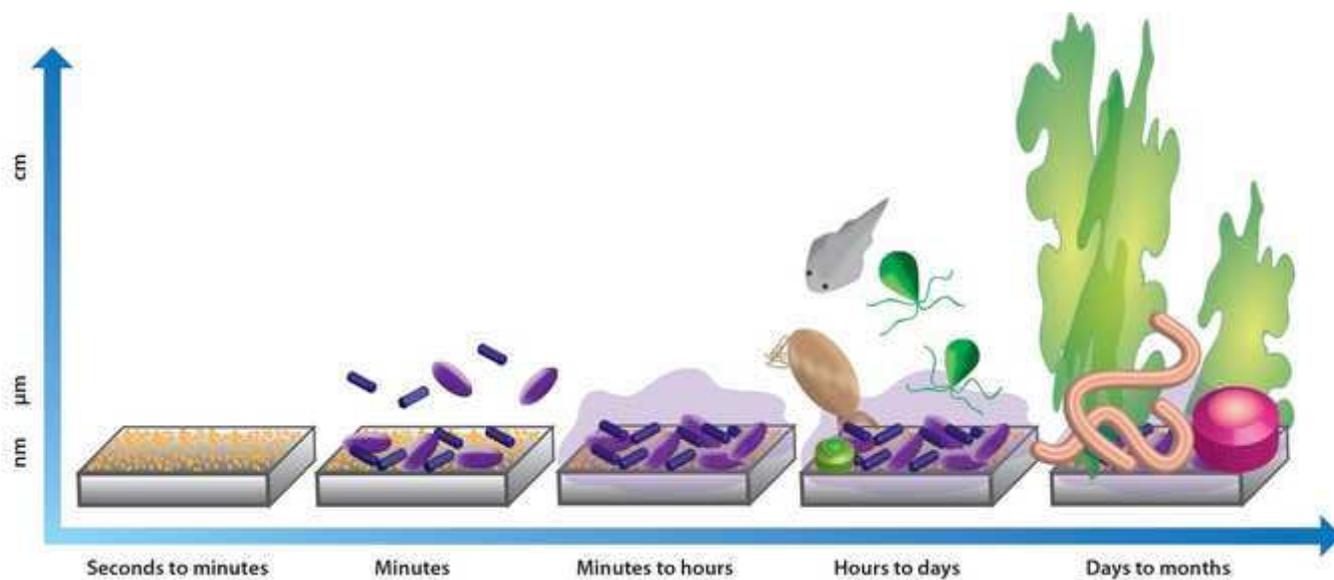
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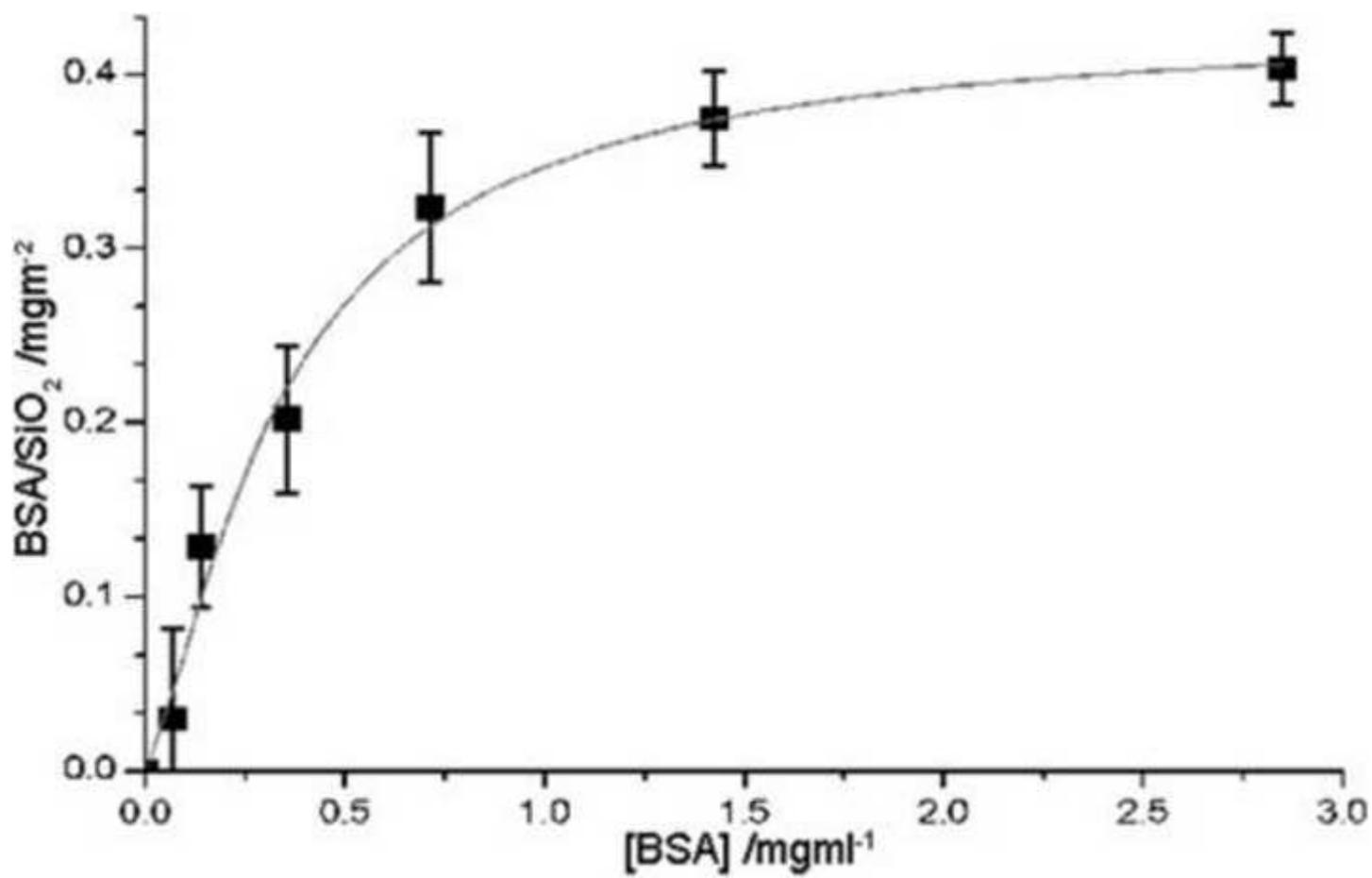
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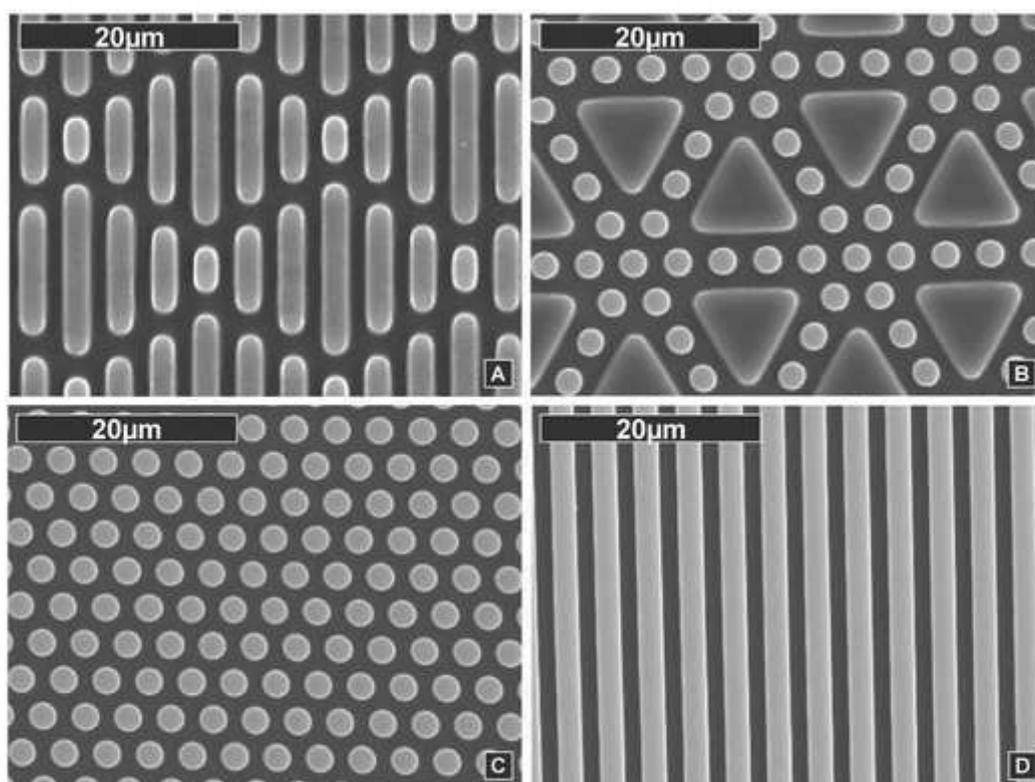


Figure 1. SEM images of engineered topographies on a PDMS surface. (A) 2 μm ribs of lengths 4, 8, 12, and 16 μm combined to create the Sharklet AFTM; (B) 10 μm equilateral triangles combined with 2 μm diameter circular pillars; (C) hexagonally packed 2 μm diameter circular pillars; (D) 2 μm wide ridges separated by 2 μm wide channels.

