Bio-inspired surface texture modification

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The imitation of natural systems to produce effective antifouling materials is often referred to as "biomimetics". Looking to the marine environment for bioinspired surfaces offers researchers a wealth of topographies to explore. Attention is given to the evaluation of textures based on marine organisms tested in either the laboratory or the field. The findings of the review relate to the numbers of studies on textured surfaces demonstrating antifouling potential which are significant. Many textures are only tested in the laboratory, where it is acknowledged a very different response to fouling is observed when tested in the field.

Keywords: biofouling ; marine inspiration ; topography ; surface modification ; antifouling

The imitation of natural systems to produce effective antifouling materials is often referred to as "biomimetics". The world of biomimetics is a multidisciplinary one, needing careful understanding of "biological structures", processes and principles of various organisms found in nature and based on this, designing nanodevices and nanomaterials that are of commercial interest to industry. Looking to the marine environment for bioinspired surfaces offers researchers a wealth of topographies to explore. Particular attention has been given to the evaluation of textures based on marine organisms tested in either the laboratory or the field. The findings of the review relate to the numbers of studies on textured surfaces demonstrating antifouling potential which are significant. However, many of these are only tested in the laboratory, where it is acknowledged a very different response to fouling is observed.

1. Introduction

Biofouling is a major problem in marine waters where most immersed surfaces become fouled to some extent, developing large amounts of biomass. Advanced biofouling in marine waters can often accumulate such significant biomass that biofouling is often further subdivided into two subdivisions; microfouling and macrofouling. Microfouling is a type of fouling composed of microbial organisms such as bacteria and diatoms. Macrofouling is caused by the accumulation of larger life forms such as barnacles, bryozoans, polychaetes and macro-algae [1][2]. Microfouling is considered a necessary precursor to the development of a macrofouling community and can be detrimental to the deployment of sensitive equipment such as environmental sensors over time scales of just two weeks in areas of high fouling pressure [3]. A search for new non-toxic marine coatings meant that the opportunity to explore "green" methods of antifouling had arisen, with the consequence that developing non-biocidal methods of preventing fouling received much attention where natural fouling defense mechanisms have been mimicked through chemical, physical, and/or stimuli-responsive methodologies [4]. In 2010 the final report of a 60-month European project: Advanced nanostructured surfaces for the control of biofouling (AMBIO) was published [5]. The team of scientists reported the study of 500 different nanostructured coatings, representing 64 generic coating chemistries that were prepared at laboratory-scale and evaluated for their antifouling and fouling-release performance. The study led to fifteen coatings selected for testing in a range of field and end-user scenarios. Several coatings showed promise, some leading to a commercialized product and others showing potential for further development [6][7][8][9][10][11][12][13][14].

Figure 1, below, shows the comparison of the growth trends looking at five key research subject areas from 2009–2019 indexed by Web of Science. Surprisingly, the subject area of biomimetic surfaces was among the least researched areas of interest during the past 10 years. This review intends to highlight some of the key contributions made in the development of antifouling solutions based solely on textured surfaces inspired by the marine environment, whilst offering some insight into those areas that need further exploration.

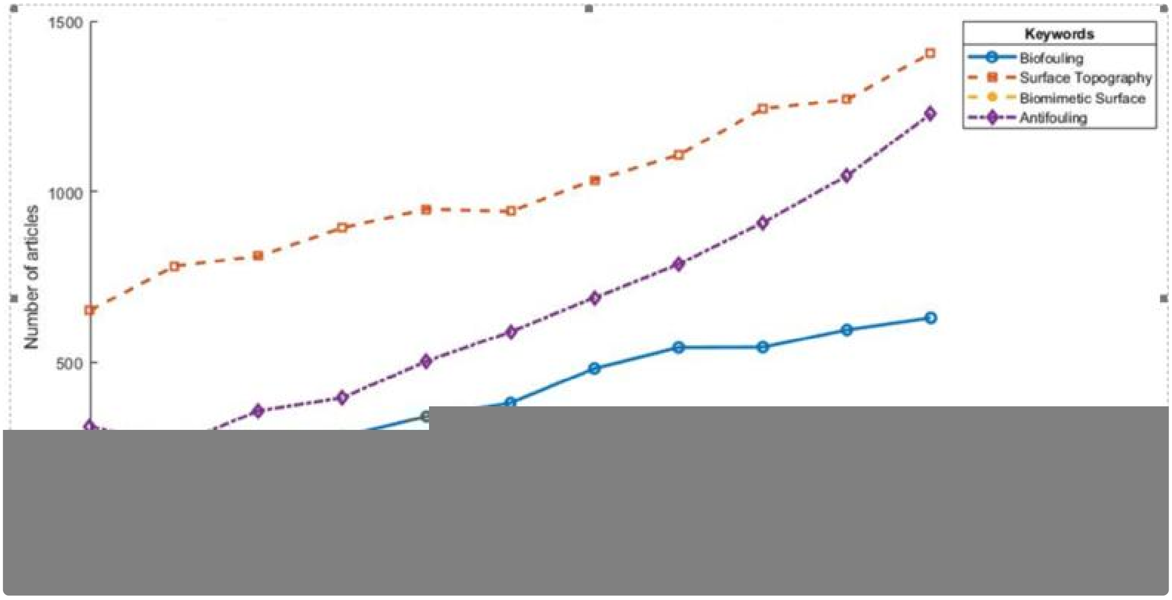

Figure 1. Comparison of the research trends of keyword selected articles from 2009–2019 indexed by Web of Science.

Biofouling is a surface-based phenomenon therefore it is not surprising that the substrate-environment interface has a significant influence on the type, rate and extent of fouling that may occur . A range of fabrication techniques is available to produce a wide variety of designed surface structures with high fidelity and relatively low-cost compared to previous decades [15]. There are extensive examples in the literature of sophisticated submicrometer scale pattern fabrication [14][16][17]. Previously, surface features were categorized as either structural topography or chemical patterning, however at the nanoscale, the distinction between purely physical and purely chemical patterning of surfaces is now being eroded. Both 3-D physical and chemical nanoscale organization are now possible within a range of methods, including but not limited to; optical lithography, microcontact printing, electron beam lithography, ion beam lithography, soft lithography, direct laser interference patterning and 3-D printing. The knowledge of nanotechnology, and with it, the ability to manipulate surface nanostructure, offers the potential to both enhance the efficacy of existing materials and to produce a completely novel, and perhaps a non-toxic mechanism of antimicrobial activity [12][18][19]. The aim of this review is to show the earliest and latest knowledge, surrounding biological responses to marine inspired surface topography. It deals with the potential of surface modification in general, and techniques used, as a viable component of future aquatic antifouling strategies.

2. Surface Modification

The study of surface topographical features has become increasingly popular, with numerous studies reporting intricate natural topographies found on many organisms that are known to resist fouling. The replication of artificial surfaces inspired by nature has produced many promising results [15][20][21][22][23]. Many studies have shown a mixture of attachment, depending on the size and shape of the organism and the specific microtexture used as a fouling-resistant mechanism. However, the explanation behind this attachment is still not well understood. A number of theoretical models have been proposed over the years to explain this attachment. One of these models is the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [24][25][26]. The DLVO theory is expressed as shown in Equation (1):

$$\Delta G^{adh}\ (d) = \Delta G^{\upsilon dW}\ (d) + \Delta G^{dl}\ (d) \quad (1)$$

where ΔG^{adh} refers to the attractive van der Waals forces, ΔG^{dl} to the electrostatic repulsion forces and ΔG^{adh} to the sum of the interaction of bacteria with a substrate [27][28][29].

The foundation of the DLVO theory is to differentiate interactions between colloidal particles or a colloidal particle and a substrate. This theory also offers an explanation behind the adhesion of algal cells to a surface. Bacteria cells range in size from 0.5–2 µm, similar to the size of colloidal particles; this theory has been extensively used in material science to explain the interactions that occur between bacteria and a substrate. Equation (1) above shows that both the van del Waals forces, ΔG^{udW}, and the electrostatic repulsion forces, ΔG^{dl}, are dependent on the distance between a cell and a surface. A later extension of this theory led to a theoretical model called the extended DLVO theory. This model accounts for hydrophobic, hydrophilic and osmotic interactions (although osmotic interactions were later said to have little effect in bacterial adhesion)[27][28][29]. The extended DLVO theory can be summarized in the Equation (2):

$$\Delta G^{adh}(d) = \Delta G^{vdW}(d) + \Delta G^{dl} + \Delta G^{ab} \quad (2)$$

where ΔG^{ab} refers to acid and base interactions [28].

Another theoretical model proposed for the explanation behind cell adhesion is that of thermodynamic theory. Thermodynamic theory expresses forces (i.e., van der Waals, electrostatic and dipole) on the basis of free energy [28]. Thermodynamic theory can be summarized by Equation (3):

$$\Delta G^{adh} = \gamma_{sm} - \gamma_{sl} - \gamma_{ml} \quad (3)$$

where γ_{sm} refers to the solid-microorganism, γ_{sl} to the solid-liquid and γ_{ml} to the microorganism-liquid free energies [28].

The basis of the thermodynamic theory relies on free energy; essentially, adhesion will occur on a surface if the free energy is negative. Unlike the conventional DLVO theory, thermodynamic theory does not care about the distance between the cell and its substrate. This theory assumes that bacterial interaction with a substrate is reversible, which may not always be the case—it does not explain the behavior observed in bacterial systems. However, it does state common observations in relation to wettability; hydrophilic surfaces will attract bacteria with hydrophilic properties and hydrophobic surfaces will attract bacteria with hydrophobic properties [24][25].

A popular mechanism used to explain the adhesion of cells to a substrate is attachment point theory [30][31]. Here, the fouling organism experiences increased attachment where there are multiple attachment points and reduced attachment when the number of attachment points are decreased. This can often be related to microtexture in the sense that highly complex topographies (i.e., whereby the microtexture is smaller than that of the organism) will not be favorable for attachment. On the other hand, where the microtexture is larger than the organism, settlement is reported to occur [32]. The work of Lorenzetti et al. confirms previously cited examples about the correlation between bacterial adhesion and a substrate [33].

Over the past number of years, developments in technologies to produce surface topographies at the micro- to nano-scale level have grown tremendously and allowed for numerous "cell-surface interaction studies" [34]. Many different surface topographies at both the micro- and nano-scale level (i.e., channels, pillars, riblets, pits) were obtained through the use of various different fabrication methods [34].

2.1. Production Methods

In order to be able to assess the organism-surface interaction, it is often necessary to replicate these surfaces for testing purposes. The work of Jinhong Fu and coworkers and Marin Steenackers and coworkers as part of the AMBIO project, has shown the development of hierarchical structures on surfaces [27][28]. Fu et al. [35] defined a controllable way to produce hierarchical micro- and nanostructured surfaces simultaneously by changing the pH. This enabled the tuning of the size range of the morphologies. The topography of the multilayer structure was fixed by thermal cross-linking and turned into a superhydrophobic surface by the chemical vapor deposition of (tridecafluoroctyl)-triethoxysilane. In a separate study by Steenackers et al. [36], self-initiated photografting and photopolymerization (SIPGP) of styrene and acrylic monomers on structured ω-functionalized biphenylthiols self-assembled monolayers (SAMs) on gold was shown. This was a three-step approach allowing the preparation of defined structured polymer brushes without the need of a specific surface bonded photoinitiator function. Polymer brushes were selectively formed on cross-linked SAM regions. The polymer layer thickness was controlled by the extent of electron-induced cross-linking and head group conversion of the SAM layer [5][28]. In a recent study, picosecond (ps) laser texturing of stainless steel was carried out by Sun et al. [37], generating micro-groove and micro-pit arrays which were tested in the laboratory in artificial seawater. The results were reported to be a fast, highly controllable picosecond laser patterning way for preparing hierarchical micro/nanostructures, combined with the chemical modification by silica sol, was proposed to fabricate the anti-biofouling stainless steel superhydrophobic surfaces (SHSs). The results of five weeks seawater immersion test showed that the specimens with SHS demonstrate significant anti-biofouling effect. It is not clear if the texture alone can provide valuable inhibition of biofouling—though the technique is worth considering due to its applicability to steel.

In addition to the elegant chemical methods of generating surface features and topographies, the growing interest in materials science, has led to a wide range of physical fabrication methods. These methods are used to replicate and/or produce textures that are inspired by either attachment point theory or by surface features of natural organisms. These are summarized in Table 1.

Table 1. Summary of manufacturing methods commonly used for the production of nano- and micro-scale textured surfaces.

Method	Description	References
Photolithography *	Formation of a pattern in a layer of photoresist which can be transferred by etching into an underlying film (Figure 2a).	[38][39][40]
Electron beam lithography *	Produces surface patterning between 3–5 nm following exposure to electron beam (Figure 2b).	[41][42][43]
Ion beam lithography*	Produces surface patterning of <100 nm due to the nature of the ion.	[41][44][45]
Proximity rolling-exposure lithography (PREL) and electrochemical micromachining (EMM) *	Produces surface patterning over a large surface area, with the ability to produce texturing of various shapes that are otherwise impossible with some of the other techniques.	[46][47][48][49]
Two-photon lithography and atomic layer deposition (ALD) *	Two-photon lithography produces 3-D complex surface topographies with resolutions of around 150 nm, however, requires a photosensitive polymer resin, preventing its use with metallic materials. ALD produces accurate uniform films, offering controllability at atomic level, wafer-scale substrates and high-aspect ratio models. The combination of the two offer a promising tribological solution in small-scale systems.	[50][51]
Soft lithography	Produces topographies at the micro- and nano-scale, using PDMS as a master template (Figure 2c).	[38][52][53][54]
Micro-contact printing *	Involves the fabrication of a “stamp” from PDMS by replica molding, the stamp is covered in ink, pressed and the solvent is left to evaporate, leaving the molecules to be transferred on to the substrate (Figure 2d,e).	[38][55][56]

Hot embossing *	Involves the use of thermoplastic polymers to create micro-patterned surfaces, involving softening the polymer, pressing the template onto the warm polymer and revealing the micro-patterned surface after cooling (Figure 2f).	[38][57][58][59]
3-D printing *	A relatively new technique offering low-cost, efficiency and fast prototyping—requires more in-depth examination.	[38][41][60][61]
Picosecond laser texturing *	Involves the texturing of stainless steel to create an AF superhydrophobic surface. Results indicated a 50% decrease in the mean microbial attachment area ratio—a significant effect in comparison to the untextured stainless steel.	[62][63]

Note: The manufacturing methods denoted with an ***** are commercially available.

Figure 2. Schematic illustrations of micro- and nano-fabrication methods. (**a**) production of micro-scale surface topographies using photolithography. (**b**) electron beam lithography. (**c**) solvent casting (i.e., soft lithography). (**d**) micro-contact printing. (**e**) direct microcontact printing. (**f**) hot embossing. (available from keaipublishing under open access journal “Bioactive Materials 3”[38]).

Controlling cellular interaction with a surface is often complex, demanding careful consideration of multiple factors such as roughness, wettability, hydrodynamics, mechanical properties and topography. Many fouling organisms (i.e., bacteria, diatoms) exist in the micrometer size range with nanometer size ranges of surface attributes. Learning to control surface topography in these micro- and nano-scale levels plays a crucial role in understanding and thus, controlling bacterial attachment and biofilm formation [38].

2.2. Surface Roughness

Early indications show that substrate roughness and topography increase the adhesion of most common fouling groups, and this is attributed to features allowing protection from hydrodynamic shear forces of removal and predation, or by increasing the surface area available for attachment. Most early studies that considered the influence of substrate roughness on fouling accumulation typically did not report any attempts to characterize the roughness scales [63]. However, the later re-evaluation of surface roughness has indicated that rather than a function of the purely passive mechanisms, active exploration of suitable surfaces for settlement leads to increased settlement on “preferred” surfaces [64]. Table 2 details the scale lengths of surface topographies commonly found on developed antifouling materials.

Table 2. Description of the different scale length topographies observed in common antifouling materials [65].

Scale	**Description**
Macrotopography; Ra > 10 µm	Surface finishes from cutting tools (i.e., grinding, turning or milling).
Microtopography; Ra ~1 µm	Important in hygienic surfaces.
Nanotopography; Ra < 1 µm	A shiny surface that appears smooth to the eye yet retains nanoscale features on the surface.

Angstrom-scale topography; 1–10 nm	Functional groups on the surface affecting the ability of a cell to sense the surface (i.e., polymer brushes, self-assembled monolayers (SAMs).
Molecular topography; molecules	Influential in surface charge and affects cell-surface binding.

2.3. Surface Wettability

Surface wettability and surface energy are important characteristics of a material in both nature and in technology development. How the nature of the topography of a given surface influences the wettability of that surface, particularly in terms of establishing (super)hydrophobic surfaces, is now well established. It is now accepted that superhydrophobicity can only be obtained by introducing a certain degree of surface roughness, that is, a low surface energy is not enough [66][67][68][69], a surface's wettability is defined by its water contact angle (WCA), described by Young in 1804 [69]. It is accepted that when the contact angle is <90° the surface is hydrophilic; when the contact angle ≥90° the surface is hydrophobic. A surface having a water contact angle ≥150° is usually classified as superhydrophobic, i.e., water repellent. Young determined that the equilibrium contact angle, θo of a liquid droplet on a flat substrate is determined by the interfacial energies, between the substrate, the liquid and its vapor (Equation (4).

$$\cos\theta_o = (\gamma_{sv} - \gamma_{sl} \mathbin{/} \gamma_{ml}) \quad (4)$$

The hydrophobicity of a smooth surface is limited by the surface's chemistry; however the wetting behavior of a surface is also dependent on a surface's topography [70][71]. Surface roughness can have a dramatic impact on the materials hydrophobicity/hydrophilicity. This effect of roughness on the contact angle was first considered by Wenzel [71]. He recognized the importance of surface roughness and proposed a modification to Young's equation, which included a roughness factor, r, defined as the ratio between the actual rough surface area and the geometric projected area. According to Wenzel's equation, a solid substrate with wetting tendency (θ < 90°) will wet more easily if its surface is rough, but, on the other hand a solid substrate with water repelling tendency (θ > 90°) will repel more when having a rough surface (Equation (5).

$$\cos\theta_r^{w} = r \cos\theta_o \quad (5)$$

However Young and Wenzel only considered chemically homogeneous surfaces. Cassie and Baxter [70] extended Wenzel's work to non-homogeneous and porous surfaces. Cassie and Baxter equations can be also applied to rough hydrophobic surfaces. Equation (6) shows that as the surface is considered as a composite of solid and air, with a contact angle of θ_r^c:

$$\cos\theta_r^{c} = f(\cos\theta_o + 1) - 1 \quad (6)$$

where f is the fraction of liquid—solid contact, the composite contact is established when θo > θc and the threshold contact angle is defined by: $\cos\theta_c = (f - 1) / (r - f)$. So, for a hydrophobic rough surface, the liquid repellency prevents the liquid from fully penetrating into the depressions of the roughness morphology. Penetration of pores will occur spontaneously only for θ < 90° [72][73]. From a self-cleaning perspective, the contact angle is not the only significant parameter for defining hydrophobicity. For self-cleaning surfaces, a low level of water drop adhesion to the surface is also important. This is the product of the WCA and the contact angle hysteresis (CAH), the difference between advancing and receding contact angles. A combination of high WCA and low CAH results in a decreased force being required to set a droplet in motion [74]. Δθ is small on a chemically homogeneous and hydrophobic surface, this means that a liquid droplet will be unstable and will slide off the substrate if the substrate is tilted (conversely, if the surface chemistry is non-homogenous Δθ will be large and the droplet will be effectively "pinned" to the substrate's surface.

2.4. Hydrodynamics

Hydrodynamic stresses play an essential role in most if not all physiological processes. In particular, cellular processes (i.e., cell morphology, intracellular processes, kinetics and cell to cell signaling) can be easily influenced by hydrodynamics [75][75]. In designing a material with an antifouling (AF) effect, a deeper understanding of the fluid mechanics at play in the micrometer to nanometer scale is essential [75]. The intertidal zone is an area in the marine environment exposed to air at low tide, and covered in seawater at high tide, leading to a huge diversity of plant and marine life [76]. It is an extremely harsh environment where the effect of a number of stresses (i.e., drag, lift acceleration) on plant and animal life are evident. In the intertidal zone, water velocities can reach between 10 and 15 ms^{-1} [77], and storm waves can reach 25 ms−1 in addition to accelerations of more than 400 ms^{-2} [78]. Hydrodynamic forces are said to have a huge effect on the ability of fouling organisms to settle. In this area of the marine environment, marine organisms are not prone to fouling, even though they are subjected to the same fouling pressures as found elsewhere. These non-fouling organisms with enhanced surface topography and optimal hydrodynamics offer an excellent opportunity to develop a non-toxic antifouling solution [76].

Reynolds number is defined as “the ratio of inertial forces to viscous forces in fluid flow”. It essentially expresses the influence of size and shape of organisms moving in a fluid [76][79]. Reynolds number can also be an indicator of the scale separation in fluid flow [79]. Microorganisms (i.e., bacteria, plankton, ciliate) experiencing Reynolds numbers of around 10^{-5} are said to be in an environment in which viscous forces dominate over inertial forces. As a result, bacteria, plankton and ciliate function at low Reynolds number [79]. These hydrodynamic interactions significantly influence the ability of an organism to settle on a surface, allowing an organism to identify a suitable surface. In contrast to this, organisms experiencing Reynolds numbers between 10^3 to 10^9 are said to be in an environment in which inertial forces dominate over viscous forces. Therefore, larger organisms and underwater surfaces operate at high Reynolds number [79]. One of the challenges in creating an effective antifouling bioinspired solution is adapting systems that are both effective at low Reynolds number (i.e., over small surfaces) as well as systems that are effective at high Reynolds number (i.e., over large surfaces). Table 3 outlines the variation of Reynolds number experienced by marine organisms with respect to speed .[76][79]

Table 3. The variation of Reynolds number in marine organisms with respect to speed.

Reynolds Number	Speed (Approx. ms^{-1})	Organism
10^{-5}–10^{1}	10^{-5}–10^{-3}	Bacteria, plankton, ciliate
10	10^{-3}–10^{-1}	Small fish
10^{3}	10^{-3}–10^{-1}	Large fish
10^{5}–10^{7}[18]	10^{-1}–10	Human swimwear, large fish
10^{7}–10^{9}	10^{-1}–10	Blue whale, large ships

Figure 1. Comparison of the research trends of keyword selected articles from 2009–2019 indexed by Web of Science.

Biofouling is a surface-based phenomenon therefore it is not surprising that the substrate-environment interface has a significant influence on the type, rate and extent of fouling that may occur [8][9][10][11][12]. A range of fabrication techniques is available to produce a wide variety of designed surface structures with high fidelity and relatively low-cost compared to previous decades [15]. There are extensive examples in the literature of sophisticated submicrometer scale pattern fabrication [14][16][17]. Previously, surface features were categorized as either structural topography or chemical patterning, however at the nanoscale, the distinction between purely physical and purely chemical patterning of surfaces is now being eroded. Both 3-D physical and chemical nanoscale organization are now possible within a range of methods, including but not limited to; optical lithography, microcontact printing, electron beam lithography, ion beam lithography, soft lithography, direct laser interference patterning and 3-D printing. The knowledge of nanotechnology, and with it, the ability to manipulate surface nanostructure, offers the potential to both enhance the efficacy of existing materials and to produce a completely novel, and perhaps a non-toxic mechanism of antimicrobial activity[12] [18][19]. The aim of this review is to show the earliest and latest knowledge, surrounding biological responses to marine inspired surface topography. It deals with the potential of surface modification in general, and techniques used, as a viable component of future aquatic antifouling strategies.

3. Conclusions

This review shows that inspiration from marine organisms has provided surface textures that have been replicated using a variety of fabrication techniques. These textures have been tested in the lab and field for their antifouling potential, with varied success. Many biofouling studies are lab-based using testing with single-celled organisms which are easier to statistically analyze and quantify. However, the success of these AF technologies is likely to be very different when applied under environmental and field conditions.

Of the surveyed papers, many of the marine organism texture features are in the micron range. These vary from 1–10 µm, 100–500 µm with few studies in the nanometer range. Few innovative techniques have been adopted for replication of surface features. The challenge is in meeting the required dimensions as these are limited by the capability of the replication technique, and also the ease of replicating from a small-scale surface to a larger scale. This has been shown to be a challenge using the techniques described in Table 1. However, innovations in roll-to-roll manufacturing can potentially realize the delivery of larger scale replicas of the structure. Micro-contact printing for example or 3-D printing are offering greater flexibility in material development. Although marine inspired surface texture and topography was the focus of this review, an effective AF solution will need to consider combining both surface chemistry, like the very elegant technique by Rosenhahn with suitable topography. While textured surfaces alone have not demonstrated complete antifouling success, evidence suggests that texture plays a significant role.

Existing studies discussed in this review, principally focus on the applicability of the topographies inspired by shark, dolphin and crustacean, for example. However, there are very few novel biomimetic natural surfaces that have demonstrated significant antifouling potential. These textures typically are very complex with hierarchical structures—varying in dimensions. Development and evaluation of fabrication methods to create or replicate patterned surfaces at both micro- and nano-scale levels is required. The replication of effective surface topographies for large scale applications remains a challenge and choice of texture is critical in achieving success. Further research on marine inspired textures with potential antifouling capability, is required to understand the mechanisms involved and the potential for larger scale application.

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