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Recent Progress of Biomimetic Antifouling Surfaces in Marine

Hao Yan, Qingshan Wu, Cunming Yu, Tianyi Zhao, and Mingjie Liu**

Marine biofouling is defined as the accumulation of living organisms on surfaces submerged in seawater. The growth of aquatic organisms on the man-made surfaces such as ships, buoys, sonar devices, and ocean infrastructures is regarded as a serious problem. Antifouling paints are developed to prevent the growth of biofouling by continually releasing biocides. In recent years, the outstanding antifouling performances discovered from natural creatures have motivated the development of new biomimetic antifouling approaches. In this progress report, the recent development of biomimetic antifouling surface is summarized. The main advantages and drawbacks of these systems are presented along with a brief introduction to their scientific basis. As the potential development of biomimetic coatings is still far from commercialization, some common yet hitherto neglected perspectives are discussed. It is believed that by selecting and combining the most effective antifouling mechanisms from nature, will bring a new era to nontoxic antifouling paints in the near future.

1. Introduction

Marine biofouling is defined as the accumulation of living organisms on surfaces submerged in seawater. The buildup of microfoulants (virus, bacteria, fungi, diatom, and algae) and macrofoulants (hydroids, barnacles, tubeworms, and macroalgae) on ships, buoys, sonar devices, and ocean infrastructures have been regarded as significant problems.[1] The most apparent detrimental effects of biofouling are increased fuel consumption of ships and more carbon dioxide emissions.[2] In order to counter the biofouling in marine, antifouling paints have been developed. By continually releasing toxic compounds into the seawater adjacent to the surface, the fouling organisms are killed before they become permanently attached.[3] Among all the different compositions proposed throughout the history, tributyltin self-polishing copolymer paints (TBT-SPC paints) have been the most successful one.[4] TBT-SPC paints are based on acrylic backbone polymers and ester linkage to TBT side groups. The carboxyl—TBT bond is hydrolytically unstable in slightly alkaline conditions, which can be controlled to slowly hydrolysis in marine. TBT-SPC paint was the first commercialized antifouling products to show a durable efficacy (>5 years) with modest cost of production. It is estimated that antifouling products provide the shipping industry with annual fuel savings of $60 billion and reduces carbon dioxide emissions of 384 million tons.[5] Soon, concerns about the high persistence and toxicity of TBT-SPC paints had emerged especially where mollusks are related. The negative impacts of TBT on the marine environment induced more and more restrictions from the governments, and finely led to their worldwide ban by the International Maritime Organization in October 2001.[6] The restriction on the use of TBT lead to a renewed use of copper and zinc-based biocides in paints. Co-biocides to copper, such as Sea-Nine 211, zinc pyrithione, and Irgarol 1051 were added to increase efficacy against algae.[1,6] Unfortunately, recent studies have shown that Irgarol 1051 may have had a detrimental effect on marine plants with a long half-life.[7,8] The negative effects of toxic substances in traditional antifouling paints stimulated biofouling studies, and increased the necessity to find "environment-friendly" methods.

In the marine environment, the binding of microorganisms to a surface can confer advantages to cell survival.[1] The sessile mode of life is widespread in a variety of marine phyla, and all require surfaces to attach on. The surfaces are similar to other resources, which are constantly competed among members of the same or different species.[9,10] According to the competitive exclusion principle, species less suited to compete for resources should either adapt or die out, which lead to the evolvement of diversity strategies to dominate the surfaces. In further, the "surface" in here should not be only considered as one of inorganic substratum, but also the outermost layer of any lifeforms which are needed to keep clean for survival.[11] By observing and investigating from the nature, different antifouling strategies have been found in many cases, such as chemical cues and biocides are synthetic by microorganisms to prevent from being colonized by macroorganisms;[12,13] Inorganic particles are picked up by water droplets due to the micro and nanoarchitecture on the lotus leaf, which minimizes the droplet's adhesion with superhydrophobic surface;[14] Some insects, such as cicadas and dragon flies, have evolved nanoprotrusions on their

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wings that can rupture and kill the bacteria on contact without damaging their transparency;[15,16] The gecko's setae help it to adhere to the wall, and when the setae are fouled with macro-particles, these particles can be removed through continuous climbing;[17,18] Fishes secrete mucus to make their bodies slimy, which can insulate the contaminants from the scales.[19–21] It can be seen that the nature has developed diversity antifouling surfaces, together with the different strategies of self-cleaning to keep the cleanliness throughout lifespan. By studying these cases, biomimetic approaches may well provide us new insights into designing and developing nontoxic antifouling paints.[22–24] In this report, the recent progress of biomimetic antifouling surfaces is discussed, together with some common yet hitherto neglected perspectives in this field regarding biofouling studies. It is believed that by selecting and combining the most effective antifouling mechanisms from nature will bring a new era to nontoxic antifouling paints in the near future.

2. Biomimetic Antifouling Surface Technologies

Traditionally, the process of biofouling in marine can be described as four main stages (see **Figure 1**).[1,9] It has to be mentioned that these fouling stages can overlap, be successional or occur in parallel. Also, the influence of inorganic matters is not discussed in the biofouling process.

Stage 1 (1 min): Organic molecules of proteins, polysaccharides, glycoproteins, and others rapidly adhered to the surface, which are essentially governed by physical forces such as Brownian motion, electrostatic interaction, and van der Waals forces. The adsorption of these molecules on the surface, also known as conditioning film, changes the physicochemical properties of the surface and affects the bacterial adhesion;[25]

Stage 2 (1–24 h): The conditioning film allows the process of diatoms and bacterial adhesion to occur. The primary adhering microorganisms, while still in the reversible stage of adhesion, and later initiating the formation of a biofilm;

Stage 3 (in a week): The existence of adhesive exudates (extracellular polymeric substances, EPS) such as polysaccharides, proteins, lipids, and nucleic acids help to trap more particles and organisms. The rich nutrients and ease of attachment into the biofilm allow secondary colonizers to attach, such as algal spores, barnacle cyprids, marine fungi, and protozoa. The formation of a microcolony with primary producers, grazers, and decomposers is complete;

Stage 4 (2–3 weeks): The tertiary colonizers complete the settlement and the growth, such as larger marine invertebrates and macroalgae.

Biomimicry is to learn from and mimics the strategies found in nature. As in aquatic and terrestrial environments, different species have evolved diversity strategies to battle for surfaces or prevent been colonized by other organisms. The mechanisms underlying different strategies can be used as countermeasures for preventing biofouling in different stages, which will be discussed in the following section. **Table 1** summarizes these methods regarding their main strategies, components, and the foulants that can resist to.

2.1. Natural Antibiotic Approaches

The biocides used nowadays prevent biofouling due to the nonselective lethal toxicity toward microorganisms and are becoming a problem to the environments.[4,6,26] By discovering that a large variety of microorganisms such as bacteria fungi, algae, and corals have developed secondary metabolite for the against of other organisms, it is possible to study and

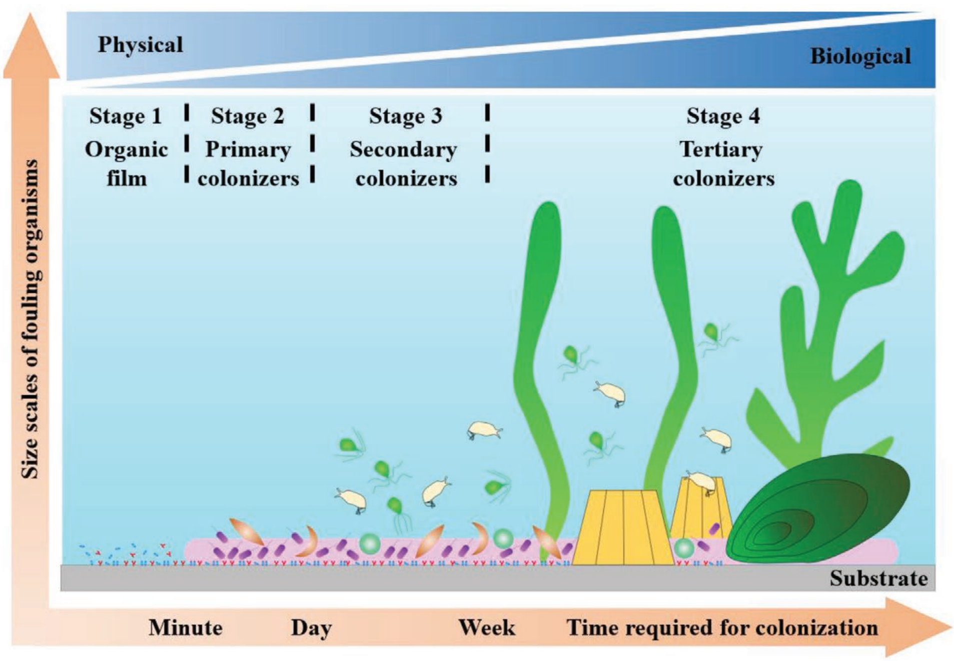

Figure 1. Conceptual illustration of biofilm development process.

Table 1. Current antifouling strategies.

Strategies	Components	Resistant foulants	Ref.
Natural biocides	Antibiotic QS inhibitor Enzyme inhibitory	Microfouling Macrofouling	[13,14,28,29,32–37]
Underwater superoleophobic surfaces	PEG-based polymers Hydrogels coatings Zwitterionic polymers	Microfouling Macrofouling Protein	[41–49,51–62]
Micro/nanopatterns surfaces	Nano/micropillars bioinspired topography	Microfouling Macrofouling	[69–89]
Fouling release coatings	Silicone Fluorinated polymers	Inorganic sediment Macrofouling	[90–105]
Other antifouling methods	Slippery liquid-infused porous surfaces	Microfouling Macrofouling Inorganic sediment	[107–113]
	Bacteria immobilized hydrogel matrix	Microfouling Macrofouling	[114–117]
	Dynamic topography surfaces	Microfouling Macrofouling Inorganic sediment	[118–128]
	TENGs-based antifouling system	Microfouling Macrofouling	[133–135]

synthesize natural antibiotic products as potential biocides.[1,13] Secondary metabolism is a term for small molecule products of metabolism that are not necessary for the organism's growth and reproduction, but help to fight against multitude of adverse situations. Antibiotic, one of the most important products of secondary metabolism, inhibits the growth of other microorganisms even at low concentrations. The compounds of butenolide, terpenoids, steroids, carotenoids, phenolics, alkaloids, and peptides extracted from the marine organisms all showed antifouling activities.[13,27] Pan et al. raised an ideology of "From the Nature for the Nature."[28] Butenolide derived from marine bacteria and biodegradable poly(lactic acid) polyurethane derived from crops was fabricated as an environment-friendly coating. Marine field test was conducted according to ASTM D6990-05 (2011) method and showed remarkable antifouling ability after immersion in marine for three months.

Quorum sensing (QS) is a mechanism for cell–cell communication and adjust gene expression in high concentration of bacteria.[12,29] It allows bacteria to coordinate functions during biofilm formation, in which acyl homoserine lactones (AHLs) are the general and most studied signals. AHLs produced by different bacteria differ in the length of the side chain and played a role in interactions between bacteria and other species in marine.[30,31] Wheeler et al. discovered that zoospores of the marine alga *Ulva* exploit AHLs to find the most suitable bacterial biofilms for settlement.[32] With the study of QS, compounds as QS inhibitor have been identified that can be used to control biofilm. For example, the addition of β-cyclodextrin which could bind to AHLs could decrease the abundance of QS signal by 75% and regulate algicidal activity.[33] Furanones and cinnamaldehyde were found to block QS system by displacing AHL from its receptor. Halogenated furanones extracted from the temperate red alga *Delisea pulchra* effectively avoids a broad spectrum of bacterial infections.[34] The antifouling activity of halogenated furanones was investigated by De Nys et al., which showed inhabitation to barnacle cyprids and algal gametes in low concentration.[35] Manefield et al. discovered that this compound could inhibit bacterial colonization and biofilm formation through blocking AHLs via competitive inhibition and destabilization of LuxR protein.[36,37]

Nowadays, the chemistry of marine natural products has become a mature field.[13] Due to the intense study of microbe–microbe interactions, microbe–algae interactions, and microbe–invertebrate interactions, numerous bioactive compounds have been found and studied. Among the producers of these compounds, algae, sponges, bryozoans, and mollusks have received most attention of academic and industrial research.[13] And these compounds have been shown to exhibit a wide array of bioactivities including antitumor, enzyme inhibitory, receptor antagonist, antiviral, and antifungal. However, it is not our intention to report this field in details, but to show a possible solution of environment-friendly biocide.

2.2. Non-Antibiotics Related Approaches

Natural products can be successfully used for antifouling applications in laboratory studies. However, to use an antifouling coating with antibiotics of secondary metabolism in the field is still a challenge. In nature, it is possible to control the formation of biofilm with different strategies other than using antibiotics, which in most cases involve adjusting the surface properties. The methodology to mimic such surfaces can be categorized as following two: The first uses chemical approaches, in which the surface is chemically modified; The second uses physical methods, wherein the surface architecture in micro or nanoscale is modified in order to inhibit the growth of microorganisms into biofilms.

The thermodynamic theory considers the surface-free energies of the solid substratum surface, the foulant's surface, and the suspending medium yielding the interfacial free energies between the interacting surfaces.[9] Accordingly, this comparison is expressed as free energy of adhesion as Equation (1)

$$\Delta G_{\mathrm{adh}} = \gamma_{\mathrm{sf}} - \gamma_{\mathrm{sl}} - \gamma_{\mathrm{fl}} \tag{1}$$

where the solid–foulant interfacial energy is denoted by γ_{sf}, the solid–liquid interfacial energy by γ_{sl}, and the liquid–foulant interfacial energy by γ_{fl}. Adhesion of foulant is thermodynamically favorable if ΔG_{adh} is negative because systems tend to minimize their free energy. The most common way to measure surface energy is through contact angle experiments. Based on the contact angle results and knowing the surface tension of the liquids, the surface energy can be calculated. The equilibrium contact angle is determined by the Young equation as Equation (2)

$$\cos\theta = \frac{\gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}}}{\gamma_{\mathrm{vl}}} \tag{2}$$

where the solid–vapor interfacial energy is denoted by γ_{sv}, the solid–liquid interfacial energy by γ_{sl}, and the liquid–vapor interfacial energy by γ_{vl}, then the equilibrium contact angle by θ. It can be seen that the surface energy measured by contact angle experiments can only represent the relationship between surface, water, and vapor. Water contact angle data, alone, are not sufficient to determine adhesive strengths of foulants. But still, the adhesion in nature is strongly correlated with substratum surface energy. The work by Baier et al. in the late 1960s demonstrated an empirical relationship between relative adhesion of fouling organisms and the free energy of the surface, which can be analyzed by contact angle measurements.[38] The data from marine and biomedical results were compiled and found that when fouling retention versus surface energy, there were two minima. One concentrated at low surface energy characteristic of silicone surfaces and the other at higher energies associated with hydrophilic polymers such as hydrogels.[39,40] The Baier curve has guided marine antifouling coating designs for many years.

It has to be noted that the Young equation assumes that the surface is chemically homogenous and topographically smooth. When it comes to any surface with patterns in nano or microscales, the apparent contact angles measured on a macroscopic scale rarely reflect the surface's physicochemical properties which foulants actually interact with.[19] So, in this section, we will be discussing underwater superoleophobic surfaces, surfaces with micro/nanopatterns, and fouling-release coatings (FRCs) separately.

2.2.1. Underwater Superoleophobic Surfaces

When a fresh surface is immersed in natural waters, conditioning film of adsorbed components (i.e., humic acid, proteins, and other organic molecules) is formed on the surface before adhesion of microfoulants as described in stage 1. This is due to that molecules diffuse much faster than microfoulants.[9] The presence of a conditioning film can change the charge and the free energy characteristics of the substratum. Such changes in substratum surface properties may influence microfoulants adhesion in different ways.[41–43] Actually, many organic macromolecules have extensive hydrophobic domains in their structure, such as proteins. If the hydrophobic character predominates, then the molecule will be expelled from the bulk water phase and accumulate at solid–liquid interfaces. Protein resistance is critical for antifouling performance, since not only the forming of conditioning film in stage 1 involves the adsorption of protein, many organisms can secrete protein-based adhesives.[1]

The physicochemical properties of the surface play an important role. The contact step of foulant is closely associated with the wettability of material surfaces, indicating that by controlling the surface wettability might be a promising way to control the fouling of oleophilic components. Numerous superwettability-based self-cleaning strategies have been adopted by different species in natural.[14] One of the famous examples is the fish scales with underwater superoleophobic property.[20,21] The scales of carps are composed of hydrophilic composition including calcium phosphate, protein, and a thin layer of mucus. Such structures can trap water layer on their surfaces, resulting in underwater superoleophobicity, thereby dramatically reducing the adhesion of oleophilic components to the material surfaces. To mimic this strategy, different methods have been developed to obtain underwater superoleophobic surfaces. Owing to the steric exclusion effect and surface hydration layer, hydrophilic polymeric materials, such as poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA), poly(2-hydroxyethyl methacrylate) (PHEMA), and poly(zwitterionic), have shown profound capability to resist nonspecific adsorption of proteins and reduce organisms' attachment.

One of the well-known underwater superoleophobic surfaces is produced with PEG-based polymer, which exhibit resistance to protein adsorption, bacterial colonization, and cell adhesion. Since the first report of oligo(ethylene glycol) (OEG) self-assembled monolayers (SAMs) coating for protein resistance, a variety of approaches, such as physical adsorption, covalent grafting attachment, and some of other techniques have been developed to attach PEG onto surfaces.[44–47] Also, different methods were made to explain the protein resistance of PEG-modified surfaces. The unique interaction between the water and the PEG chain results in the formation of a surface hydration layer and creates a steric hindrance to the coming proteins. When proteins attempt to approach hydration layer, the first step is expulsion of water molecules from both surface and protein. This would require arising free energy barrier from dehydration entropic effects.[48] Ishihara and co-workers found that the amount of nonfreezable water around polymer chains may influence the degree of protein adsorption resistance.[49] By investigating the design parameters of PEG brushes, Nalam et al. found that the grafting densities and the molecular mass of polymer brushes could define the number of water molecules associated with Schilp et al. investigating the effect of PEG chain length and terminal groups for antifouling efficacies, and concluded that PEG with long chain length exhibited better antifouling efficacy than OEG (see **Figure 2**).[50,51] Strategies such as grafting cyclic or dendritic polymer structures

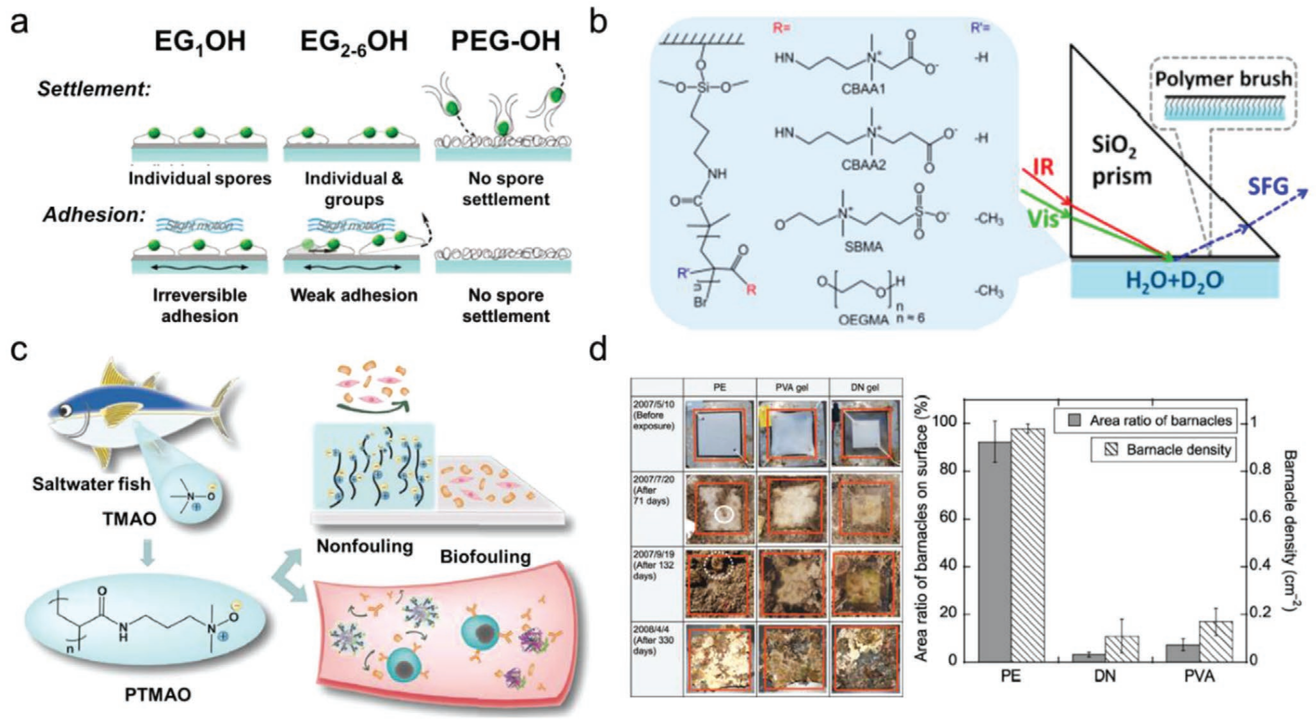

Figure 2. a) The different responses of spores of *Ulva* to OEG and PEG surfaces. Reproduced with permission.[51] Copyright 2009, American Chemical Society. b) SFG measurement of the pCBAA1, pCBAA2, pSBMA, and pOEGMA polymer brushes on a right angle silica prism in contact with isotopically diluted water. c) The design of polytrimethylamine N-oxide (PTMAO). A new class of ultralow fouling bioinspired materials. Reproduced with permission.[62] Copyright 2019, American Association for the Advancement of Science. d) Area ratio and the density of barnacles settled on various surfaces after exposure for 330 d. Reproduced with permission.[57] Copyright 2019, Taylor & Francis.

could prevent solvent-induced chain stiffening and maintain high surface hydration, thus maximizing the antifouling properties of coatings. High mobility and large exclusion volume of the PEG chains also contributed toward the overall antifouling performances. However, in spite of excellent antifouling properties, the ether bonds in PEG could be autoxidized easily in presence of oxygen and susceptible to thermal degradation. These problems may limit PEG-based polymers and its oligomers to be used for long-term applications.[52]

Hydrogels mostly consist of water and cross-linked hydrophilic polymer networks, which have also been studied for antifouling applications.[53] Ulbricht' group synthesized a series of hydrogels based on poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) and found that PEGMEMA-based hydrogels have low protein sorption and bacteria deposition tendencies.[54] This indicated that PEGMEMA-based hydrogels could be used as fouling-resistant materials. Rasmussen et al. tested the settlement of *Balanus amphitrite* cyprids larvae on different hydrogel surfaces.[55] The results showed that alginate, chitosan, polyvinyl alcohol substituted with light-sensitive stilbazolium groups (PVA-SbQ), and agarose hydrogel surfaces inhibited barnacles' settlement compared to the polystyrene control. PHEMA/BCl hydrogel fabricated by Cowling et al. also exhibited excellent resistance to marine microfouling for five months.[56] In order to improve the application time and mechanical properties of antifouling coatings, Gong's group prepared a tough poly(2-acrylamide-2-methyl-1-propanesulfonate) and polyacrylamide DN gel which could maintain antifouling properties in the marine environment for 330 d (see Figure 2).[57] Due to the presence of great number of cross-linked hydrophilic polymers, the antifouling mechanism of hydrogel could be maintained with longer stability.

Zwitterionic polymers including carboxybetaine, sulfobetaine, and phosphorylcholine can be categorized as another series of underwater superoleophobic surfaces.[58] In numerous studies, zwitterionic polymers coating in lab assays showed profound antifouling abilities to different organisms such as alga, diatoms, *Ulva*, barnacle, etc.[48] The key to their outstanding anti-biofouling properties is the nanometer-scale homogenous mixture of balanced charge groups since both are strongly hydrated through ionic salvation. Compared to the hydration of PEG and hydrogel coating via hydrogen bonding, the electrostatically induced hydration by zwitterionic polymers is more pronounced. And it is more difficult for the proteins to absorb onto the surface of zwitterions coating.[59] For a better understanding of the interfacial water structure of zwitterionic polymers, Jiang's group used sum frequency generation (SFG) vibrational spectroscopy to provide structural information at the molecular level (see Figure 2).[60] Zwitterionic, poly(oligo ethylene glycol methacrylate) (pOEGMA) brushes, PMMA, and poly(ethylene terephthalate) (PET) were tested with SFG, and results showed that only strongly hydrogen-bonded water molecules were observed on the zwitterionic surfaces, whereas the surface hydration of pOEGMA contained a small amount of weakly hydrogen-bonded water. For the other two polymer samples without antifouling properties, SFG signals only show weakly hydrogen-bonded interfacial water molecules. Xiang et al. carried out umbrella sampling and molecular dynamics (MD) simulations, and showed that the higher grafting density sulfobetaine brush array exhibits a more organized structure which can hold a tightly bound hydration water layer at the interface.[61] Compression of this hydration layer results in a strong repulsive force. However, at a lower grafting density, the brush array exhibited a randomly oriented structure in which the repelling of the brush array was through the deformation of the sulfobetaine branches. These results demonstrated zwitterionic brush arrays with different grafting densities posed different antifouling mechanisms.

There are only three major categories of zwitterions, which limits the scope of application of zwitterionic antifouling coatings currently. Therefore, studies have been made to search for new types of zwitterions. Inspired by protein stabilizer trimethylamine N-oxide (TMAO) which was discovered in saltwater fishes (see Figure 2), Li et al. reported a new class of TMAO-derived zwitterionic polymers (PTMAO), which could achieve an ultralow protein adsorption in undiluted blood serum.[62] Besides, the researchers also combined some specific functional materials with zwitterions to expand their applications. Jiang' group prepared poly(2-(2-((2-(methacryloyloxy) ethyl) dimethylammonio)acetoxy) benzoate) (PCBSA) polymers which consist of an antimicrobial leaving group salicylic acid (SA).[63] Through hydrolysis of ester bonds, the antimicrobial SA was released. This composited platform kept the surface free from bacteria and inhibit bacterial growth. Silver nanoparticle (AgNP) as a releasable antibacterial agent was desirable to incorporate into the zwitterionic hydrogels to prevent bacterial colonization and subsequent wound infection. GhavamiNejad et al. used catecholic chemistry to synthesize antimicrobial silver nanoparticles impregnated into antifouling zwitterionic hydrogels.[64] The prepared composite hydrogel exhibited good antimicrobial activity against both Gram-negative and Gram-positive bacteria. Moreover, zwitterionic peptides have recently emerged, which have been shown to form a stronger hydration layer compared to PEG in some contexts. And which could be synthesized in monomer-level precision by protein engineering with recombinant approaches. Therefore, zwitterionic peptides were also an ideal candidate for antifouling materials. Walker et al. fabricated antifouling surface coatings based on recombinant expression of zwitterionic EK peptides.[65] These coatings demonstrated that the recombinant production of polymers to form thin film coatings incorporating surface attachment, antifouling, and functional antibody-binding motifs was feasible. These efforts that integrated silver nanoparticles or zwitterionic peptide also broaden the application of zwitterions.

However, some researches of the zwitterionic polymers antifouling performances in the field tests showed opposite results with the laboratory ones. Yandi et al. investigated the antifouling abilities of cationic (PDMAEMA), anionic (PSPMA), neutral (PHEMA-*co*-PEG10MA), and zwitterionic (PSBMA) brushes with laboratory assays to protein adsorption; attachment of the marine bacterium; settlement of zoospores of the green alga; settlement of barnacle cyprids; and field immersion tests.[66] In laboratory conditions, neutral and zwitterionic surfaces showed superior inhibition to most of the foulants. But during the first week of field immersion tests, cationic and anionic surfaces showed better antifouling properties. And all samples were fully fouled after immersion for eight weeks, no significant difference could be distinct between each other. Koc et al. found similar results with custom-made sulfobetaine- and sulfabetaine-bearing zwitterionic copolymers thin hydrogel films. The antifouling tests in lab suggested that not only the hydration layer incorporation but also the attachment geometry of the zwitterionic side chains would enhance the antifouling behavior.[67] But the antifouling effect of such coatings failed when performing field tests in the marine.[68] More detailed examinations revealed that the accumulated foulants in field tests were mainly composed of inorganic compounds and diatomaceous soil sediments. Further simulating field tests in the laboratory confirmed that inorganic particulate matter could accumulate on hydrophilic coatings and impair the antifouling performances in no more than 10 min (see **Figure 3**). This is an intriguing result in which the influences of inorganic sediments have seldom been discussed in most of literatures involving biofilm or antifouling studies. To solve this problem, self-generating and self-renewing strategies were proposed to modify zwitterionic surface.[69–71] Dai et al. designed copolymer containing the hydrolysis-induced zwitterionic monomer tertiary carboxybetaine triisopropylsilyl ester ethyl acrylate.[69] Due to the rapid hydrolysis abilities, the hydrolyzed polymer chain can be dissolved into seawater, leading to a self-renewing dynamic surface (see Figure 3). This method has shown potentials to solve the problems now underwater superoleophobic surfaces are facing, and more results on long-term performances in field are needed.

2.2.2. Surfaces with Micro/Nanopatterns

Unlike bees, which can use the grooming structures on their limbs to clear out the attached pollens or parasites on their wings, most cicadas as well as other "large-winged" insects have extremities that are too short to clean the wings.[11,72] As seen in **Figure 4**, cicadae, planthopper, and dragonflies have developed their own antibacterial strategies with periodic nanopillars on the wings.[16,73–75] Ivanova et al. proved that the bactericidal surface activity was not determined by the chemical properties of the nanopillar, and proposed a physicomechanical mechanism that the high-aspect-ratio nanopillars ruptured and consequently killed the bacterial cells upon adhesion.[76] Unlike cicada and dragonfly wings that have shown only efficient bactericidal properties to Gram-negative bacteria, wings of *Diplacodes bipunctata* were found to have the ability to kill both Gram-negative (*Pseudomonas aeruginosa*) and Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) bacteria.[16] Inspired by these findings, black silicon (bSi) bactericidal surface with high aspect ratio nanopillars was synthetized by reactive-ion etching technique. The nanostructured bSi sample generated a mechanical bactericidal effect, which is highly effective against all tested Gram-negative bacteria, Gram-positive bacteria, and endospores. Kelleher et al. compared the bactericidal efficiency of the wings of three different cicada species with different heights, diameters, and spacing.[15] The results show that the nanopillars with the largest height, smallest diameter, and spacing were most effective in killing Gram-negative bacteria

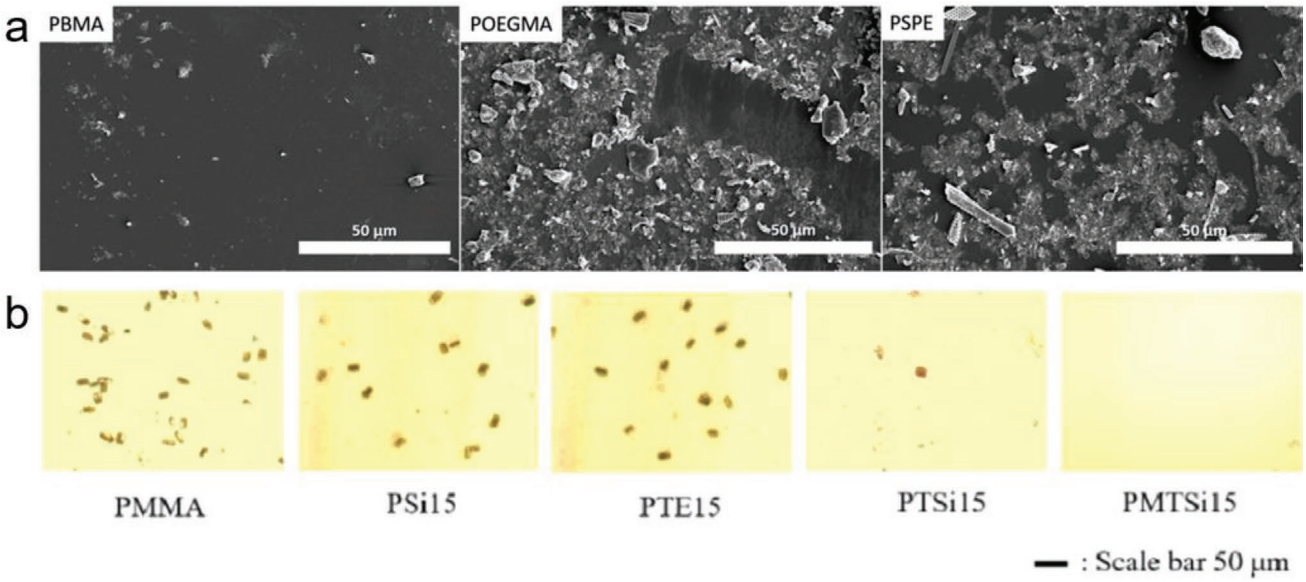

Figure 3. a) SEM images of the three coatings immersed for 10 min in autoclaved sediment. Reproduced with permission.[68] Copyright 2019, Taylor & Francis. b) Photograph of the diatom *Navicula incerta* on copolymer surfaces with prehydrolysis for 3 d after 24 h of immersion. Reproduced with permission.[69] Copyright 2019, American Chemical Society.

(*Pseudomonas fluorescens*). Later on, Pogodin et al. supported the hypothesis with a biophysical model to explain the interaction of bacterial cells with nanopillar structures.[77] When bacteria was adsorbed onto the nanopillar structures, the cell membrane stretches in the regions suspended above the pillars. And the cell membrane will be eventually ruptured if the degree of stretching is sufficient.

The unique properties of cicada and dragonfly wings have drawn many research interests to mimic the physical nature of bacterial killing. This strategy provides an effective method to prevent the formation of biofilms while negating the current need of using antibiotics or other chemical agents, which is a great benefit to be adopted in medical implant devices and in marine.[78–83] Recently, Jenkins et al. proposed new findings in

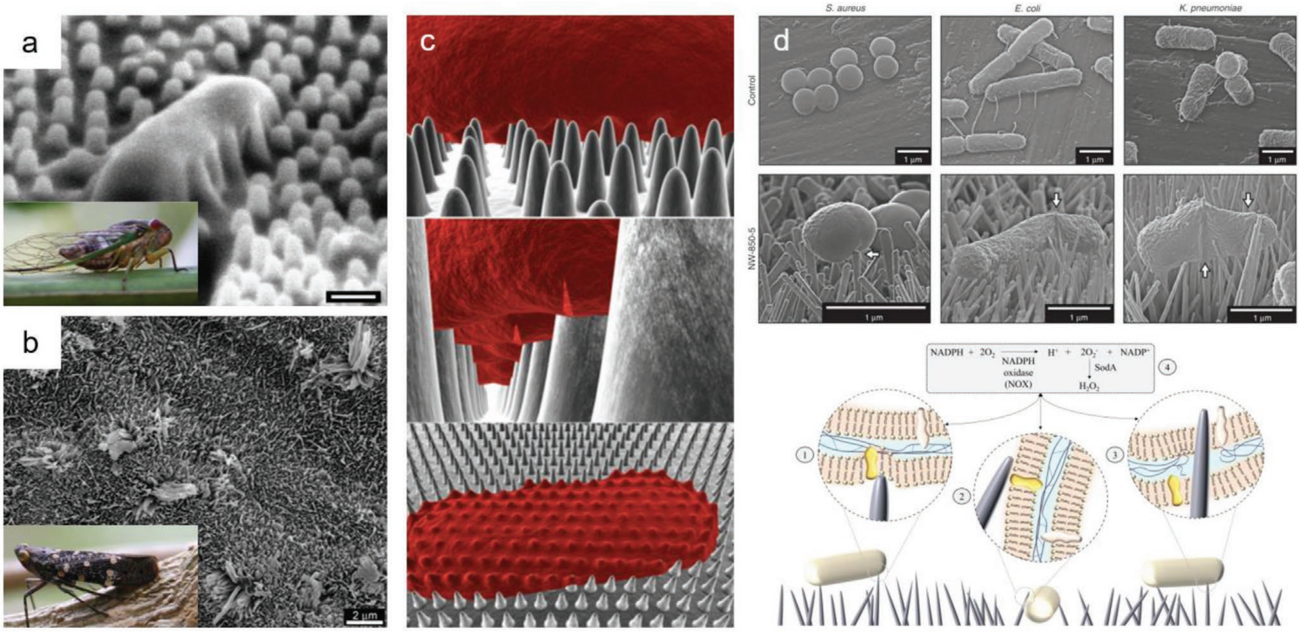

Figure 4. a) Photos and SEM images of cicada, *Psaltoda claripennis*. Reproduced with permission.[73] Copyright 2019, Wiley-VCH. b) Digital photographs and SEM images of the Northern Queensland native planthopper, *Desudaba danae*. Reproduced with permission.[74] Copyright 2017, American Chemical Society. c) Biophysical model of the interactions between cicada wing nanopillars and bacterial cell. Reproduced with permission.[77] Copyright 2013, Elsevier. d) Determining bacterial morphology on nanopillar surface using SEM and proposed antibacterial mechanisms of TiO_2 nanopillar surface. Reproduced with permission.[84] Copyright 2020, Springer Nature.

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the research to this area (see Figure 4).[84] By detailed examination of Gram-negative (*Escherichia coli* and *Klebsiella pneumoniae*) and Gram-positive (*Staphylococcus aureus*) bacteria contact with titanium dioxide (TiO_2) nanopillars substrate, both deformation and penetration to the envelope in three bacteria can be found. Interestingly, mechanical rupture or lysis of bacterial cells by nanopillars has not been found. The relatively low frequency observed in envelope deformation and penetration could not be account for the reductions of bacterial viability compared to controls. Thus, the physiological response triggered by nanopillars was studied with proteomic and reactive oxygen species analysis. And the results provide a possible explanation that the nanopillars increased abundance of bacterial oxidative stress, which reduced the capacity of bacteria to proliferate.

In nature, a wide variety of animals and plants with nanoscale topographic features on the surface were discovered. For a better understanding of the surface structures evolved from nature, Schroeder et al. provided a detailed review of the specialized structures in insects for adhesion, movement, interaction with water, and for sensing and production of optical, thermal, vibrational, and chemical signals.[72] Similarly, plant surface structures in different environmental conditions, with detailed micro- and nanostructures descriptions, were summarized by Koch et al. (see **Figure 5**).[85,86] The topographical cues such as surface roughness, waviness, and pattern aspect ratio have all shown significant effects upon bacteria adhesion behavior. The adhesion process can be influenced when surface topography of a scale is comparable with the cell dimensions. Patterns of natural *Trifolium* and three other kinds of leaves were replicated with silicone elastomer by Wan et al.[87] The antifouling performance was studied with nonmotile microalgae, which are able to sink into the trenches. The replica of *Trifolium* leaf covered with dense microspines with about 2 µm length and 0.3 µm width showed lower microalgae settlement compared to other kinds of leaf replicas with no distinct microstructures. Surface topography in marine organisms also attracts research interests. Bers and Wahl replicated crab (*Cancer pagurus*), blue mussel (*Mytilus edulis*), sea star (*Ophiura texturata*), and the egg case of dogfish (*Scyliorhinus canicular*) with epoxy, and revealed a variety of surface textures with different antifouling effects on the settlement of invertebrate larvae.[88] Scardino et al. studied 36 mollusk species fouling with 12 weeks, and characterized surface topography by scanning electron microscopy (SEM) and light microscopy.[89] The results showed that the highest waviness profiles having the weakest fouling adherence, and the relationship between other surface structure parameters and fouling resistance properties were rather complicated within different microorganism species.

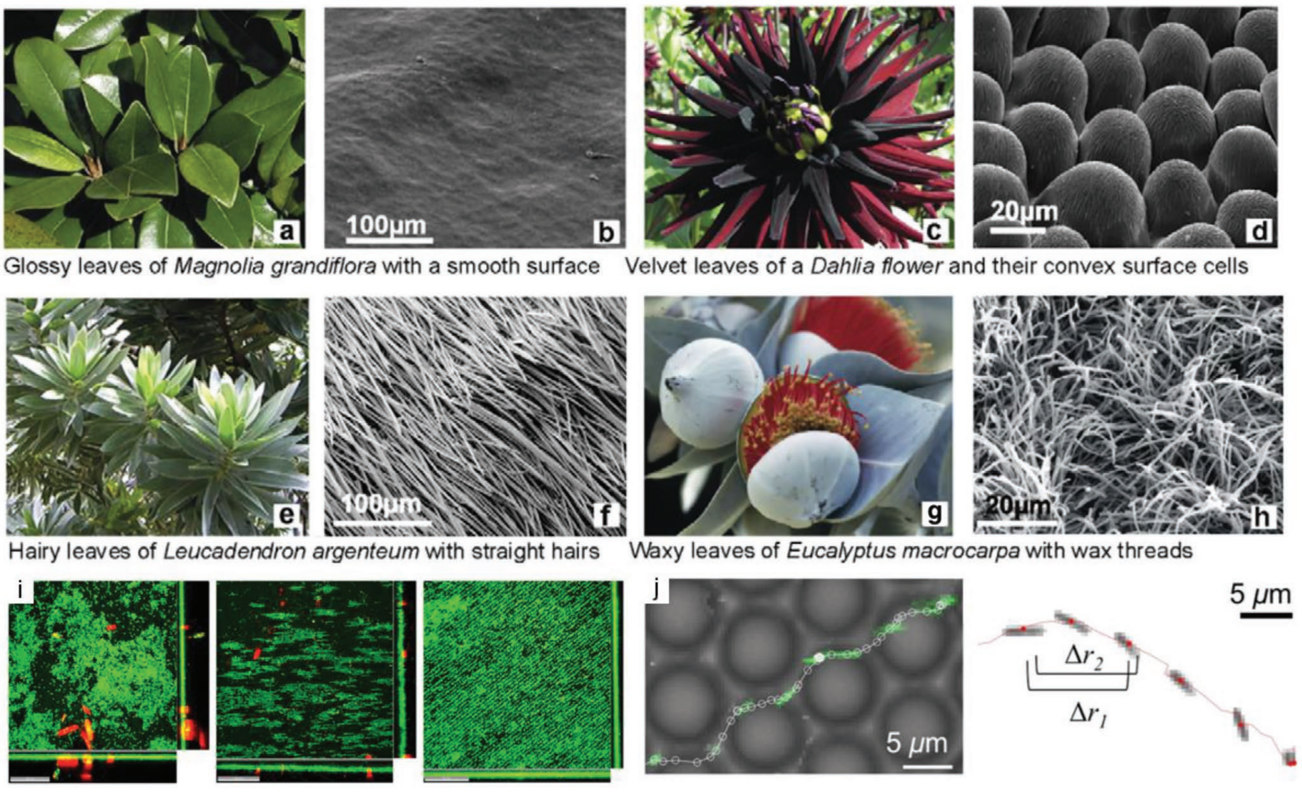

Figure 5. Macroscopic appearance of plant surfaces and their surface microstructures. a) The leaves of *Magnolia grandiflora*. b) SEM image of *Magnolia grandiflora*. c) The flower petals of *Dahlia*, d) with convex structured cells. e) The silvery appearance of the *Leucadendron argenteum* leaves. f) SEM image of the dense layer with light reflecting hairs. g) The leaf and flower bud surfaces of *Eucalyptus macrocarpa*. h) SEM image of a dense covering with thread-like wax crystals. a–h) Reproduced with permission.[85] Copyright 2009, Elsevier B.V. i) Representative CLSM images of the marine biofilms on different microfabricated PDMS surfaces (groove widths with 0, 1, and 2 µm). Images contain green fluorescent signals indicating live cells and red fluorescent signals indicating membrane-compromised cells. Scale bars represent 30 µm. Reproduced with permission.[96] Copyright 2014, Taylor & Francis. J) Time-lapse imaging of bacterium (green) traversing an 8 µm textured surface. Reproduced with permission.[97] Copyright 2018, American Chemical Society.

Microorganisms that lived in marine are always influenced by flow conditions, and thus hydrodynamics plays a significant role along the adhesion process. By using computational fluid dynamics (CFD) simulations, Halder et al. proved that the surface topography at the micro and nanoscale has considerable influence on the near-surface flow condition, which affects different biological activities of microorganisms in relation to their reversible settlement.[90] Sharks, one of the fastest swimmers in marine, have been intensively studied in biomimicry.[91–94] Shark skin is covered with numerous small dermal tooth-like elements, and varied among species. The denticles structure and their possible effect on the pattern of water flow over the body is believed to prevent the adhesion of microorganisms. Inspired by the antifouling properties of shark skin, a commercialized product Sharklet Antifouling with topography consisting of rectangular ribs with designed spacing and height was presented by Brennan's group.[95] This biomimetic topography fabricated with poly(dimethyl siloxane) elastomer has proven to effectively reduce attachment of spores of *Ulva*, diatoms (*Navicula incerta* and *Seminavis robusta*), and cyprids (*Balanus amphitrite*). By reducing the ribs' width and spacing to 2 µm, *Ulva* (≈5 µm) settlement reduced by 86% compared to a smooth surface (see Figure 5).[92]

These experiments implied that surface topographies pose different effects to different species, the width and spacing of topographical features should be tailored based on different demands.[96] Also, the ability to move on solid surfaces provides ecological advantages for organisms. Chang et al. discovered that the surface motility of bacterium could be hindered by surface topographical features (see Figure 5).[97] These results help to elucidate more mechanisms by which surface topography influence biofilm formation. However, biofilms are always composed of multiple species, cohabiting with or competing against each other. The antifouling performance of the natural surfaces' replicas on certain fouling organisms decreased over time. Such finding reported that the repulsive effect of microtopography began to decrease after four weeks.[1] Bacteria, fungi, and algae in biofilms excrete EPSs to enhance adhesion, thus changing the surface topography by filling or covering surface features.[89] Since the species investigated above do have a combination of antifouling strategies such as molting and burrowing, it is suggested that the patterned surfaces as one potential method should not be designed as the only features in the antifouling coatings.[71] Extensive researches are needed to find new methods to combine different strategies into one antifouling coating.

2.2.3. Fouling-Release Coatings

In nature, not every animal can prevent from being colonized by organisms, such as crabs, turtles, and even some giants. Gray whales and humpback whales are a few of the biggest mammals in ocean, and they are famous of being covered with lice, worms, and wiggly barnacles. As for their relatives, the skin of porpoises and killer whales all show excellent antifouling abilities. It is suggested that their skin have low surface energy, which can provide low drag and remove foulants with hydrodynamic stress during swimming in high speed.[98–100] Unlike antifouling coatings that can inhabit the adhesion of foulants, ** FRCs do not actually prevent the organisms' attachment.[94] However, the combination of low surface free energy, low roughness, and low elastic modulus together lead to low interfacial bond between organisms and the FRCs. Even if organisms manage to attach on the surface, only weak dispersive interactions will take place, resulting in the easy removal of the organism from the substrate by water jet or hydrodynamically self-cleaned when sailing at higher speed. The concept of FRCs is one of the most promising nontoxic antifouling alternative strategies.[101]

Actually, FRC is not a recently discovered method. Unfortunately, SPC based on TBT had shown overwhelming success on antifouling performances, which made FRCs more as sidelined products in the early days of antifouling market.[101] Not until the ban of using TBT, non-biocidal measures to control biofouling regain the interest, of which FRCs are the most practical. Up to now, more than ten companies are providing different types of FRCs products.[101] Most of these coatings are based on silicone elastomers, and few are fluoropolymers. To further enhance the performance of silicon-based FRCs, adding lubricant oils is the most common method. In the early 1970s, a patent of adding low molecular weight silicone polymer into commercially available silicone elastomers to enhance fouling-release properties had already been published.[102] Callow et al. reported that silicone elastomers containing methylphenyl silicone oils could improve antifouling performance than the ones without oils.[103] To study the depletion of the oil from the FRCs coating into the marine, Truby et al. radiolabeled oils and repeated this experiment in more test sites for two years.[104] The data showed similar results that the addition of oil could decrease the adhesion of some species of invertebrates. Less than 1.1 wt% of the infused oil leeched from the coating over one year, and <1.1% and <0.08% of the total labeled oil was found in water and sediment, respectively. The relatively slow loss of oil from FRCs suggested that the impact on environment may not be as severe as SPC-TBT products can cause. Nowadays, the incorporation of oils are common additives but not explicitly mentioned in commercialized products.[101,105] From a research by Nendza,[105] the requirements for the speeds of ships are not identical between different products and mostly requires speed higher than 10 knots.[101] As for underwater structures and ships during idle periods or low cruising speed of travel, FRCs are particularly susceptible to fouling. Diatoms are well-known for being more favorable to hydrophobic surfaces, and the adhesion strength with FRCs is strong enough to resist removal even at high hydrodynamic stress. Schultz et al. reported on the development of a fully turbulent flow channel for assessment of adhesion strength of microorganisms, and wall shear stress in the test section can be varied from 0.9 to 30 Pa.[106,107] Based on this design, Holland et al. studied the adhesion strength and motility of diatoms attached to different surfaces.[94] Compared to polydimethylsiloxane (PDMS), diatoms could be removed more easily from glass. As for *Navicula*, which adheres to PDMS much strongly, cells could not be removed completely even at the highest wall shear stress that the water channel apparatus could output (53 Pa). After 2 h settlement, the complete removal of *Navicula* cells required a water jet with surface pressure of 275 Pa, which was equivalent to the wall shear stress of a ship sailing at the speed of 35.5 knots.

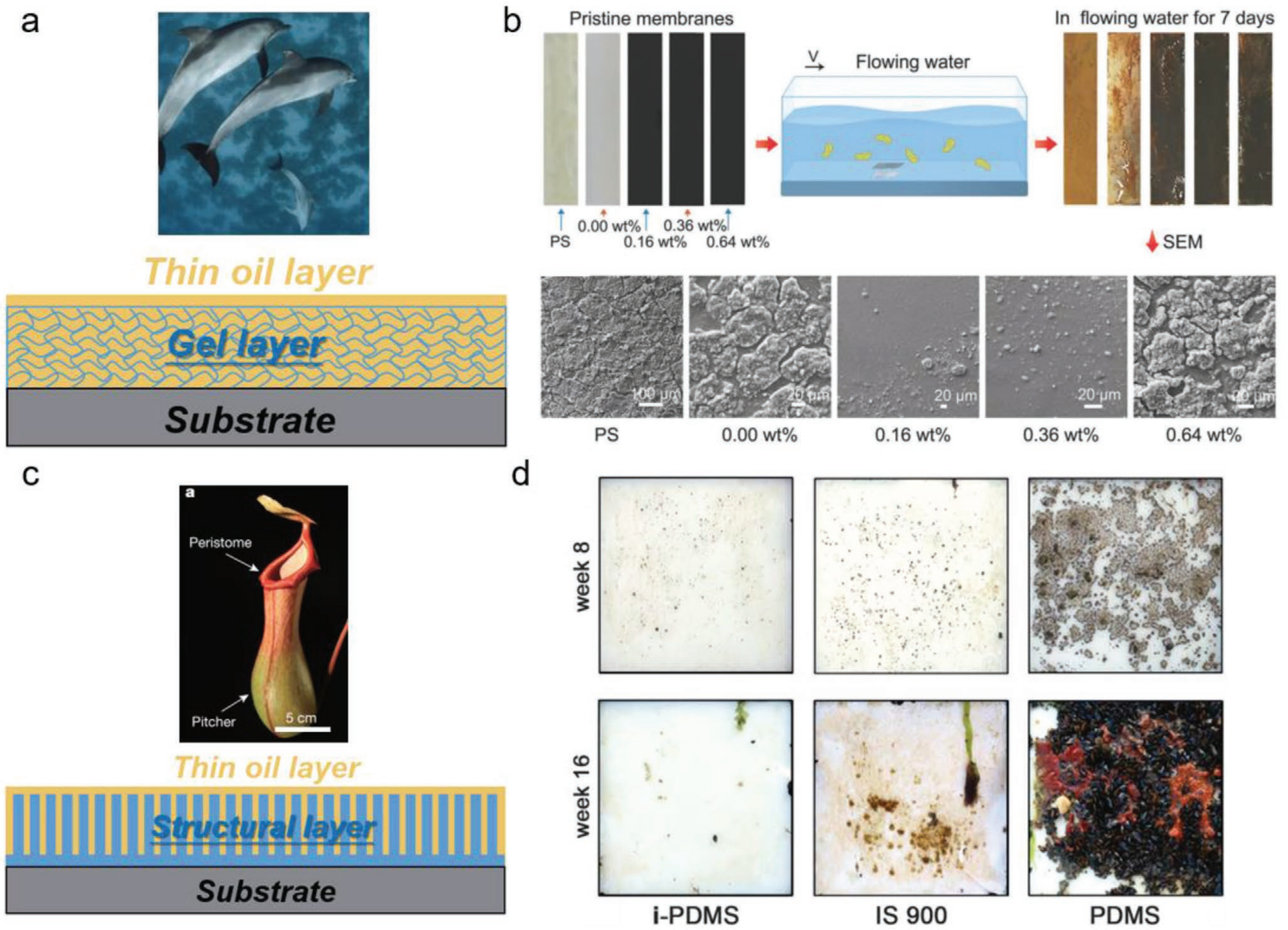

Figure 6. a) Image of dolphins, which inspired the fouling-release coating and the scheme. Reproduced with permission.[162] Copyright 2014, Springer-Verlag, Berlin, Heidelberg. b) Comparison of the specimens with different modulus in flowing water; SEM measurement of the specimens after bacterial attachment test under hydrodynamic conditions. Reproduced with permission.[112] Copyright 2019, Royal Society of Chemistry. c) Image of *Nepenthes alata*, which inspired the SILPS coating and the scheme. Reproduced with permission.[116] Copyright 2016, Springer Nature. d) Representative images for the fouling communities associated with SILPs and control panels after 8 and 16 weeks of static immersion at Scituate Harbor, MA. Reproduced with permission.[120] Copyright 2017, American Association for the Advancement of Science.

Besides the low surface energy, the low elastic modulus also plays an important role in FRC.[108–111] By varying cross-link density with functional silicone oligomers with degrees of polymerization, PDMS elastomers with modulus values between 0.2 and 9.4 MPa were synthesized by Chaudhury et al., and the effect of modulus on the release of adhered spores of alga *Ulva* was investigated.[108] The data revealed significant increase in percentage spore removal under low modulus. This can be explained that PDMS films of low modulus are prone to elastic hydrodynamic instability. Under hydrodynamic conditions, micrometer-scale deformations on the elastic surface were discovered by Jin et al. (see **Figure 6**).[112] By measuring a PDMS elastomer coating (elastic modulus = 0.56 MPa) with a laser sensor, 5 μm deformation can be found under the flow rate of 1.5 m s^{-1}. The bacterial attachment test in flowing water confirmed low Young's modulus is beneficial to reducing biofouling with harmonic motion effect. Later Bing et al. developed this result by constructing more complex structures with graphene-silicone elastomers.[113] While under a fluid flow of 0.5 m s^{-1}, a maximum deformation of 0.3 μm and a response frequency of 10 Hz were discovered. This behavior could introduce instability with harmonic motion effect and fouling release performances. However, the decrease of elastic modulus will lead to mechanical abrasion, which reduce coating efficacy over time. The coating stiffness must be sufficient to maintain durability requirements during lifespan. Hence, extremely soft materials would not be suitable in real scenario. Commercialized antifouling silicone elastomers such as RTV11 or Intersleek have been reported with the modulus in the range of 3–1.4 MPa, and finish coat of FRCs is suggested to be refreshed every five years.[114]

2.3. Other Antifouling Methods

2.3.1. Slippery Liquid-Infused Porous Surface (SLIPS)

Recently, SLIPS inspired by the slippery surface of *Nepenthes* has attracted tremendous amount of attention due to its superior water repellency.[115,116] First report by Aizenberg's group demonstrated that the presence of an immobilized liquid layer of fluorinated oil on polytetrafluoroethylene surface could significantly reduce biofilm attachment under static conditions or gentle flow.[117] Later they found similar trend in oil-infused PDMS samples than noninfused ones.[118,119] But the adhesion to immobilized liquid layers on surface is different to each species and strains, due to different cell surface structures, such as adhesins, flagella, and imbriae.[120] As seen in Figure 6, Deng et al. discussed that the differences between SLIPS and conventional methods lie in the state of the lubricant liquid inside the paint.[121] Despite the surfaces made by these two methods are all covered with a thin layer or oil, the fluid phase inside SLIPS is located in the pores of the solid structures, while the material swells with the liquid to form a homogeneous phase in the case of an oil-impregnated paint. A company named Adaptive Surface Technologies was later spun out from Harvard's Wyss lab. Long-term field tests have been carried out around the globe, and the former product using SLIPS technique has shown similar performance to the traditional FRCs. By the incorporation of amphiphilic group onto the surfaces, the second generation of SLIPS coating showed improved static performance and excellent dynamic release abilities (>10 knots) than traditional FRCs over one year.

Although SLIPS coating has been shown as an appealing solution for the biofouling problems, concerns about the released oil on the marine ecology impacts emerged. Silicone oils have shown high adsorption and immobility to sediments in combination with major persistence for biodegradation. Unlike the banned tributyltin which is extremely toxic to nontarget organisms, perfluoropolyether and silicone oil may cause physical–mechanic effects with trapping and suffocation of organisms upon coating. The impacts of these lubricants on the ecology system in the long run are still under investigations. Due to concerns around the environmental safety and the high carbon footprint of the production of synthetic oils, plant oils such as argan oil, castor oil, or coconut oil have been considered as suitable candidates for the replacement.[115]

2.3.2. Bacteria Immobilized Hydrogel Matrix

Hydrogel can be used not only as antifouling paints but also as a biologically active polymer matrix to entrap living bacteria. The signaling molecules produced by selected bacteria could control the subsequent adhesion and attachment process of fouling organisms. This behavior broadens the hydrogel coating with additional antimicrobial properties. Holmström et al. found that immobilized *E. coli* cells could maintain their viability in the PVOH gels for as long as two months.[122] *Pseudoalteromonas tunicate* is a marine bacterium which has been found to produce extracellular compounds active against different classes of fouling organisms. By entrapping this bacterium into PVOH hydrogel as "living paints," the samples were inhibitory against larvae for a period of up to two weeks. This result indicated that the hydrogel immobilized with bacteria could be used for the antifouling or antibacterial applications. Interestingly, this strategy has not drawn attentions in the field of antifouling researches. Later, Akid et al. reported alternated method of sol-gel coating mixed with immobilized microbe in the anticorrosion field.[123] Two bacterial strains, *Pseudomonas fragi* and *Paenibacillus polymyx*a were loaded in the sol-gel coating system to study the anticorrosion performances on Al substrate. The examination of the field tests showed the coating with bacteria provided significant corrosion protection for more than six months. Eduok et al. continued the research on mild steel and discovered axenic thermophilic strain of *Bacillus licheniformis* showed anticorrosion/antifouling properties when loaded in sol-gel coating.[124] The field test in Gulf sea of high salinity marine environment showed the sample loaded with living bacteria and corrosion inhibitor (zinc molybdate) exhibited best anticorrosion/antifouling performances. Further examination showed that by loading these bacterial endospores, the hydrophobicity of the coating increased thereby preventing the diffusion of ions through the coating to the metal surface and increased the fouling release effect. In a recent report, Suleiman et al. found that combining both corrosion inhibitors and protective antifouling bacteria in the sol-gel coatings showed different results from laboratory and field.[125] The sol-gel coatings containing bacteria alone showed best antifouling properties, and such difference is caused due to the changes in salinity of rainwater.

2.3.3. Dynamic Topography Surface

How to clean the biofouling is also studied. Biofilms are kept together by weak physicochemical interactions of EPS.[1] The forces used in the cleaning need to overcome those interactions that are active in adhesion of primary organic material and pioneer cells. Shivapooja et al. developed dynamic change of surface area and topology of elastomers in response to external stimuli including electrical voltage, mechanical stretching, and air pressure (see **Figure 7**).[126] Detachment of bacterial biofilms and macroorganisms from dynamic surfaces can be achieved. In a later work, field studies showed more than 90% of biofilm from fouled surfaces could be released.[127] Compared with laboratory-grown biofilms, a higher strain change was required to remove biofilms accumulated in the field environments. Although this method may not be practically feasible to use in ships as antifouling coating products, it still showed potential applications for underwater infrastructures. Inspired by the dynamic undulatory topographical motion of *Batoidea*, Ko et al. designed dynamic controlled surface with magnetic field-based actuation (see Figure 7).[128] The antifouling assay was tested with *E. coli* in lab. The results showed that when sufficient deformation of the surface is induced, greater vortices and larger wall shear stress can prevent initial bacterial attachment. Shape-memory polymers (SMP) can return from one state to another shape induced by an external stimulus, usually temperature change.[129–132] By changing the shape and dimension of topographic patterns, the biofilm attached to the surface can be cleaned. Gu et al. designed a hexagonal patterned SMP substrate, and proved effective for the removal of established biofilms of multiple species when triggered surface topography changes.[131] Wrinkling has been considered as one of the most ubiquitous topographic patterns observed in nature (artery, ureter, and skin), which are also facing constant

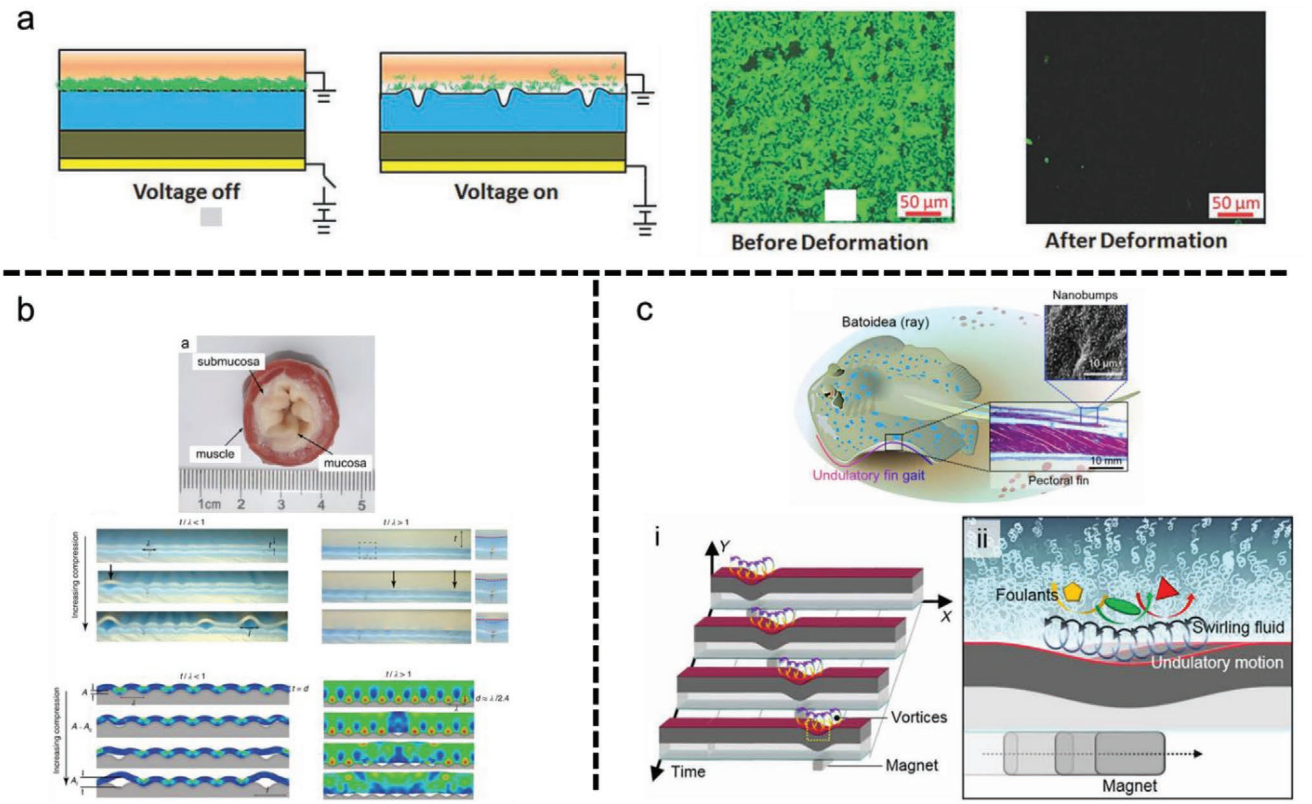

Figure 7. a) Detachment of bacterial biofilms from dielectric elastomers under voltages, and over 95% of the biofilm adhered to the elastomer detached by deformations. Reproduced with permission.[126] Copyright 2013, Wiley-VCH. b) Representative images for experimental soft silicone patches on wrinkling surfaces and finite-element simulations. Reproduced with permission.[135] Copyright 2018, Springer Nature. c) Conceptual illustration showing the undulatory gait of the Batoidea's pectoral fin together with the histological cross section of the pectoral fin, and schematic illustrations showing i) the propagating undulatory topographical wave along with the translation of the magnet and ii) the topographical wave-induced sweeping of foulants. Reproduced with permission.[128] Copyright 2019, American Association for the Advancement of Science.

threat of biofouling.[133,134] These natural surface topographies often change or actuate between wrinkling and unwrinkling state as a function of driving forces. Pocivavsek et al. proposed a mechanism of antifouling in which actuation occurred from a smooth to a wrinkled surface, and induced topography-driven delamination.[135,136] By repeating surface actuation, "self-renewing" surface can prevent buildup of foulant continually (see Figure 7).

2.3.4. Triboelectric Nanogenerators (TENGs)-Based Antifouling System

Not only to clean oneself with consuming its own energy, utilizing energy from nature is also favored. How to maximize the usage of different sources of energy to maintain cleanliness could be a strategy to gain advantage in the competition of nature. From the viewpoint of energetics, Amador and Hu classified the cleaning strategies in nature as two categories: 1) nonrenewable cleaning strategy, such as wet-dog shaking and brushing with bristled appendages; 2) renewable cleaning strategy, such as lotus effect and leaves cleaned by the wind.[11] In marine, one of the most abundant renewable energy is the ocean currents, which is estimated to be about 5000 GW in total around the globe. How to harvest energy from ocean and make use for antifouling is an interesting topic. TENGs can harvest ambient mechanical energy and convert it into electric energy.[137] By using TENGs as the self-powered energy source, electronic sensors and devices may work continuously without the need of using batteries.[138–140] As seen in **Figure 8**, Zhao et al. constructed a TENG to power a wetted insulating surface with oscillation of electric potential.[141] Significant antifouling efficiencies against different species such as bacteria and diatom can be achieved. Interestingly, the antifouling efficiencies can be further enhanced by increasing the roughness of the surface with micro/nanostructures. Feng et al. fabricated a paper/PVDF-based TENG, which can be powered by both water and wind, and can be used for cathodic anticorrosion protection and antifouling protection for algae.[142] Not only microorganisms but also the settlement of invertebrate larvae can be prevented from the oscillation of electric potential.[143] Up to now, works that are based on utilizing ambient energy are limited; the good news is that there is no evidence of any negative impacts on the ecology system. The self-powered antifouling system can be a practical antifouling solution for many marine infrastructures in the future.

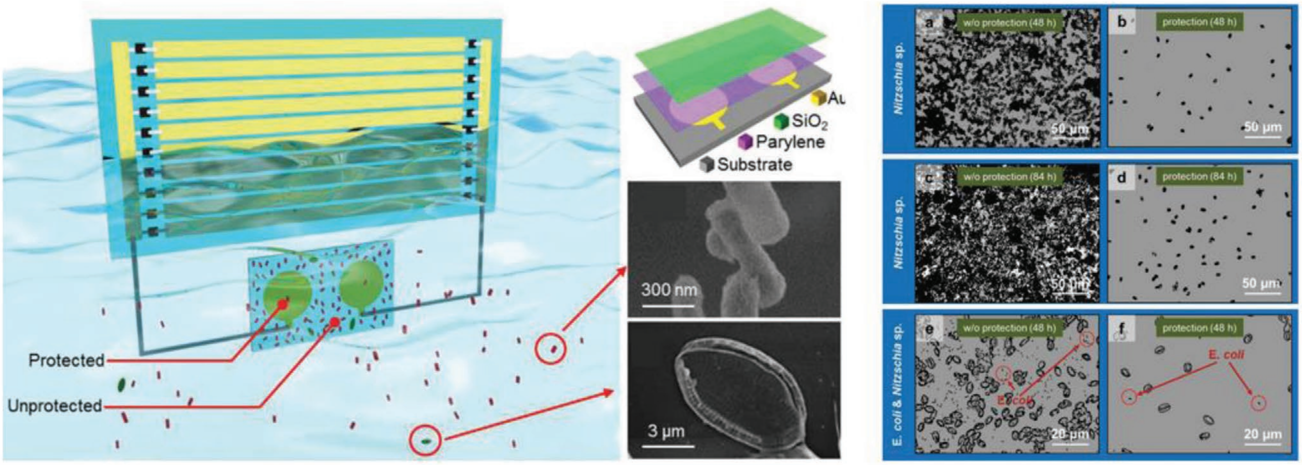

Figure 8. Setup of the self-powered antiadhesion system and antifouling results against different microorgannisms. Reproduced with permission.[141] Copyright 2016, Wiley-VCH.

3. Some Perspectives

Although many strategies based on biomimetic approaches have shown antifouling properties in laboratory assignments, few succeeded in field tests as commercialized products. In this section, we are going to discuss some of the common yet hitherto neglected perspectives for this controversy. As all surfaces in marine are constantly washed by flows, hydrodynamic interaction has been considered as one of the major contributors for the near-surface accumulation of microorganisms.[144] However, the fluid mechanics near surfaces are substantially different from in bulk fluid.[145,146] The no-slip boundary condition assumes that at a solid boundary, the viscous fluids will have zero velocity. Thus, flows near surfaces are often characterized by a significant velocity gradient, which is referred to as "shear."[147] On the other hand, the hydrodynamics at the scale of microorganisms is also different from the macro ones. Microorganisms swim in an environment of very low Reynolds number (*E. coli*, Re ≈ 10^{-5}) .[22,144] As a result, microorganisms are controlled with more viscous forces than inertial forces (low Reynolds number regime). Owing also to the nearly neutral buoyancy of most microorganisms, attractive or repulsive forces produced by large values of shear may influence the trajectories of objects near surface with different flow–microbe interactions.[148,149]

Rusconi and Stocker researched on the consequences of the forces and torques associated with fluid flow on bacteria.[150] In microfluidic experiments, fluid shear had caused strong spatial heterogeneity of motile bacteria. The magnitude of the bacteria's depletion in low-shear regions was severe due to "trapping" in high-shear regions. This result suggested that the hydrodynamic environment encourages sessile over free-swimming lifestyles, which may directly affect bacterial fitness and should be carefully considered in the study of antifouling studies. In a later review, Rusconi and Stocker summarized effects of flow on individual cells in dilute suspensions.[147] The hydrodynamic microbial processes near surfaces are very distinct from those in bulk fluids. 1) Shear-enhanced surface colonization: Shear can enhance bacterial colonization of surfaces via shear-trapping as just been discussed;[150] 2) Upstream swimming: With study of *E. coli* under different flow conditions, Kaya and Koser characterized different behavior of flow-assisted orientation (see **Figure 9**).[151] Under no-flow conditions, the bacteria exhibited circular swimming trajectories. This is because when the flagellum of a bacterium rotates, the cell body needed to counter-rotate to ensure that the net torque on the organism is zero. This rotation caused a torque that continuously reorients the cell's swimming direction producing a circular trajectory. But when the flow was changed to a moderate shear rate, the bacteria quickly aligned facing upstream and swimming toward upstream continuously; 3) Upstream twitching: Twitching motility is a form of crawling bacterial motility using hair-like filaments called type IV pili (see Figure 9).[152] When attached bacteria are exposed to increasing shear rates, it was found that cells could move against moderate fluid flows by twitching motility. This behavior is important during the formation of biofilms, in which motile bacteria are able to interact with secreted EPS.

However, most of the antifouling studies neglected the importance of hydrodynamic interactions. The experiments under static conditions or flow in labs may not be accurate enough to give a comprehensive understanding of how antifouling coatings will perform in the fields.[147,153] Drescher et al. argued that the standard assay for growing biofilms in the laboratory abstracts from these realistic environments by typically using no flow or a pump to maintain a constant flow rate.[154] It is unclear to what extent these results are relevant in natural habitats, as the standard assays neglect the interactions with other species, and physical constraints of natural environments. To give a demonstration of this question, they designed a microfluidic system that combines two shared features of *P. aeruginosa* habitats, i.e., a sequence of corners and a flow driven by a constant pressure. The results showed that in this system biofilm streamers were responsible to rapid clogging transitions, and they can cause a much stronger disruption of flow than wall-attached biofilms (see Figure 9). These findings indicated that the performance of antifouling coatings should be investigated with hydrodynamics under field conditions more closely.

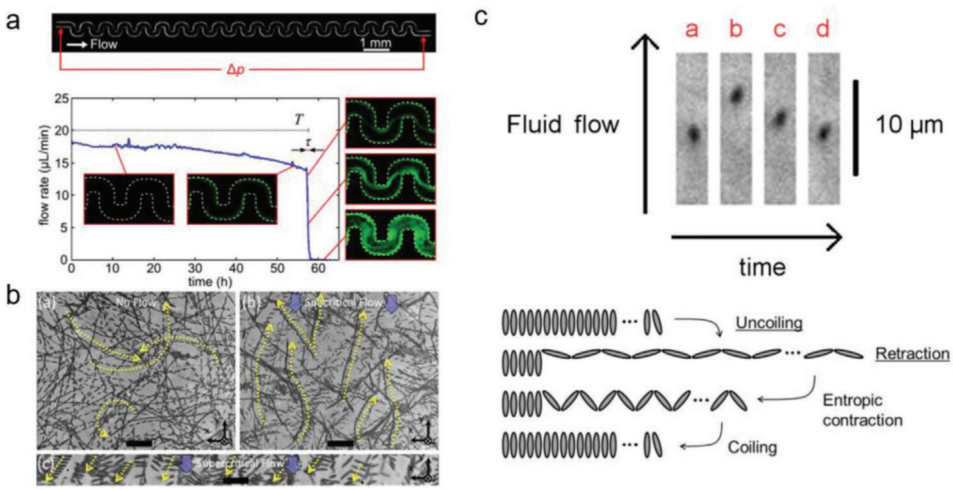

Figure 9. a) Experimental results of biofilm streamers expanded rapidly and caused clogging over a short time. Reproduced with permission.[154] Copyright 2013, National Academy of Sciences. b) Under no-flow conditions, the bacteria exhibited circular swimming trajectories, and when the flow was changed to a moderate shear rates, the bacteria quickly aligned facing upstream and swimming toward upstream continuously. Reproduced with permission.[151] Copyright 2012, Biophysical Society. c) Kymograph of microscope images of an attached bacterium moving against flow, and conceptual illustration showing the changes in the structure of pili for uncoiling and the two regimes in bacterial retraction. Reproduced with permission.[152] Copyright 2013, Public Library of Science.

Nowadays, many antifouling studies deal with different species of microorganism or macroorganism separately, while investigations of biofilms and biofouling communities received less attention. Every biofilm evolves through space and time, ranging from single layer of bacterial cells to multilayer biofilms containing numerous species.[155] Its development consists of multistep process depending on the properties of the substratum and environment. Only with the initial cell attachment and adhesion, the properties of the substratum are important. Once biofilm has formed, the underlying surface has little effect on development. On the other hand, changes in environmental conditions will immediately change the composition of biofilms and the production of chemical compounds.[156,157] Multiple studies have shown that bacteria could produce different compounds at different salinities, which would influence the cyprids temporary adhesive.[158–160] Additionally, the influences of inorganic sediments should also take into account the antifouling studies.[68]

Another possible explanation is that the power of nature selection is underestimated. Bitton classified the interaction between microorganisms and substratum surfaces by different types of interaction forces: adhesion, immobilization, and retention.[9] As for most of the references we discussed previously, most are related to the interaction of adhesion and immobilization, whereas, in fact, in many biofouling problems retention is more important. Retention of adhering microorganisms denotes microorganisms that remain adhered on a substratum surface after application of an external force. Owing to the vastness in fouling species in marine, with preferential adhesion and breadth in size and rigidity, some of these microorganisms can retain nontoxic antifouling surfaces in the end.[35] Over generations, these microsurvivors will occupy the surface and grow as dominant species in biofilms. As nature never relies on only one defense line but on integrated approaches, it is important to mimic the strategy from nature with a complete antifouling system rather than a single layer of coating.

4. Conclusion

In recent years, more advanced characterization techniques and computational fluid dynamics software have emerged, which allows more perspectives to study the strategies that nature has evolved for antifouling. This requires more professional trainings for a deeper understanding in each field. On the other hand, interdisciplinary collaborations are more and more common in different areas of science community nowadays. And antifouling is a complex system problem which requires integration of knowledge from various disciplines. The AMBIO project (Advanced Nanostructured Surfaces for the Control of Biofouling) funded by the European Commission is an excellent example.[161] The project couples the scientific expertise of different disciplines, such as polymer chemists, surface scientists, hydrodynamists, microbiologists, and marine biologists together to find alternatives to biocide-based antifouling technologies. Furthermore, the future development of biomimetic antifouling coatings also requires more deep collaboration between academic and industrial researchers.

The natural evolving process has led to the development of diverse strategies on battling for surfaces. Through the study of numerous biological cases in nature, biomimetic approaches have provided new insights into designing nontoxic antifouling coatings. Unfortunately, antifouling coating markets nowadays are still dominated by SPC paints, which are based on the release of biocidal copper and booster biocides. Only few products based on biomimetic methods can be found in the market with satisfactory field assessments results. The explanations for this controversy need more close examining. And we believed that by selecting and combining the most effective antifouling mechanisms from nature, it is possible to bring a new era to nontoxic antifouling paints in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

antifouling, biocides, biomaterials, biomimetic, organisms, surface energy

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