ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

Biomimetic Constructions of Stable Antifouling Surfaces

Manxi Wang[1,*], Taoyu Wang[2,*], Yixin Zhang[3,*], Yuhong Zhu[4,*]

[1]School of Chemistry, Sichuan University, Sichuan, Chengdu 610065, China.

[2]School of Chemical and Engineering, Dalian University of Technology, Liaoning, Dalian 116024, China.

[3]Queen Mary University of London Engineering School, Northwestern Polytechnical University, Shaanxi, Xi'an 710000, China.

[4]School of Polymer Science and Engineering, Sichuan University, Sichuan, Chengdu 610065, China.

*These authors contribute to the work equally and their names are arranged in alphabetical order of the last names.

Abstract

The demand for developing stable antifouling surfaces has surged in recent years. With the exploration of nature, much attention is given to the anti-fouling methods that could be mimicked for practical applications. Inspired by nature's structures and surfaces, many novel, bio-compatible and environmental-friendly materials and methods have been developed to solve problems associated with fouling. An overview of two types of fouling: biofouling and inorganic fouling is provided firstly. Then this review presents the broad range of antifouling strategies in the form of membranes, films and coatings inspired by different natural systems. In this review, these natural systems with extraordinary properties include tiny molecular structures existing in fauna, zwitterionic functionalities found in membrane structures, superhydrophobic surfaces and some other functional surfaces of animals. These strategies are discussed from the point of view of natural systems' abilities to inhibit contamination adsorption, followed by the antifouling mechanism in each of these strategies. Next come the physical and chemical modifications, the creation of micropatterns on the surface to control the surface textures making them antifouling. The experimental results of antifouling in each of these strategies and their implementation are also illustrated.

Keywords

Fouling resistance, bio-inspired materials, nature membranes zhangyixinncbiomolecules, nature surfaces.

1. INTRODUCTION

Solid fouling has an undesirable effect on many applications. For instance, in medical applications, biofouling happens due to the contamination caused by microbes [1]. It can occur everywhere and every moment and poses significant health risks. In order to reduce the harm caused by it, antifouling technologies are urgently needed. The unique self-cleaning and antifouling characteristics of different living organisms in nature have aroused people's great interest. Many strategies exist in nature, which use various physical and chemical control mechanisms such as low drag, low adhesion, wettability, microtexture and chemical secretions to control contamination [2].

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

Some antifouling lessons are shown in Table 1 and Table 2. In this paper, several biological mimicking designs are illustrated. By mimicking the molecules, flora and fauna in nature, scientists can produce biomimetic functional materials with excellent antifouling properties and apply them in engineering applications to solve a variety of problems.

Table 1. Flora antifouling mechanism from nature [2]. (Adapted from Gregory D. Bixler et al.)

Type	Mechanism
Lotus	Superhydrophobic self-cleaning surface
Jewelweed	Hydrophobic surface
Water fern	Superhydrophobic surface
Eelgrass	Zosteric acid secretions
Lady mantle	Hydrophobic surface
Broccoli	Superhydrophobic surface
Red seaweed	Bacteria message manipulation
Coralline algae	Shading, chemical secretion, and shedding/sloughing
Seaweed	Chemical secretions
Indian cress	Hydrophobic surface

Table 2. Fauna antifouling mechanism from nature [2]. (Adapted from Gregory D. Bixler et al.)

Type	Mechanism
Human	
Red blood cell	Phospholipid bilayer membrane
Cornea	Eyelid wiper and chemical secretions
Birds	
Dove, pigeon, duck	Superhydrophobic features
Insects	
Dragonfly, lacewing	Hydrophobic wax-covered wings
Soybean aphid	Hydrophobic mushroom-like spines
Butterfly, cicadae	Superhydrophobic wings
Molluscs and crustaceans	
Blue mussel	Microtexture and filter feeding
Crab, crawfish, lobster	Microtexture and self-grooming
Corals	
Gorgonian sea fans	Microtexture, surface energy, sloughing and mucus
Marine mammals	
Pilot whale, common dolphin	Microtexture, surface energy and enzymes
Echinoderms	
Brittle star, sea urchin	Sloughing and mucous
Fish	
Shark	Low drag, riblets, flexion of scales and mucous
Dogfish egg case	Parallel ridge microtexture surface
Fish scales	Hierarchical scale structure
Stonefish	Skin sloughing

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

2. ANTIFOULING TECHNOLOGIES

There are many different kinds of pollution existing in nature. In this section, biofouling and inorganic fouling are discussed in detail.

2.1. Biofouling Formation

Biofouling forms because of the microorganisms and their secretions. Microorganisms use extracellular polymer substance (EPS), an adhesive, to attach to one another and the substrate. Biofilms attract more microorganisms through chemical "information", continue to grow, and become more diverse. Colonization is a process in which organisms gather and grow on a surface. The five stages of colonization which include initial attachment, irreversible attachment, initial growth, final growth, and dispersion3-5 were illustrates in Figure 1. Biological flocculation growth rate depends on the organism, matrix, flow velocity, shear stress and temperature. In terms of the toughness of the biofilm, biological membrane plays an important role. Biological adhesive process could be divided into two stages including the physical adhesion and the secretion of the EPS. The first stage starts from the initial adhesion. The irreversible attached initial adhesion, i.e. adsorption, depends on the physical adhesion between substrate and microorganism. The original colonists attached to a surface through Van der Waals force. The second stage is accomplished by the secretion of EPS, which is manifested as a spongy matrix. This adhesive adheres microbes to each other permanently and attaches them to the surface [3].

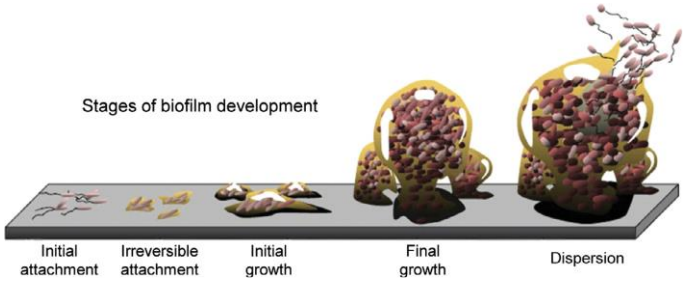

Figure 1. The formation of biofilms. The diagram shows the five stages of colonization process. Image reproduced from D. Davis et.al [4].

2.2. Inorganic Fouling Formation

Nonbiological particles form the inorganic fouling. It may attach to or independent of the biofilm. The types of particles derived from a serial of natural process such as crystallization. Inorganic dirt includes particles, frozen and airflow particles. Particle contamination occurs when suspended solids are deposited on the heat transfer surface. When the waxy hydrocarbons are in contact with the cold pipe wall, scaling and crystallization will deposit in the cold area of the oil pipeline. Airflow particles include mineral, organic and inorganic which can be commonly found in oil or gas combustion system can lead to contamination in gas pipelines, reactors, combustion chambers, and heat exchangers [5].

3. ANTIFOULING SURFACES INSPIRED BY BIOMOLECULES

There are many effective antifouling surfaces in nature, ranging from the cell membrane [4] to the lotus leaf, which protect organisms from the intrusion of pollutants. In this section, we introduce some antifouling strategies mimicking the biomolecules which typically have an anchoring domain. By covalently binding a hydrophilic chain, these molecules can be converted to antifouling coatings, membranes and then protect the substrate from organic matter fouling including oily wastewater emulsions, cellular and proteinaceous fouling. Also, some innovative changes in the fouling resistant domain have been designed, such as applying zwitterionic

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

polymers or cation polymers to modify the non-ion chain to improve the ability to fouling resistance.

3.1. Lubricin

Inspired by these biological surface structures, a series of coating materials have been designed and applied to water and oil separation, drug delivery, and implanted medical devices. Lubricin protein (LUB) is one of the important molecules in mammals' joint synovial fluid [3]. It has a unique molecular structure composed of three different blocks (the hydrophobic ends are positively charged and in the middle is a highly negative mucin-like domain) [2]. LUB has good lubrication and adsorption resistance so that it can effectively prevent joints from inflammation caused by frictional wear and pollution and provide good joint function.

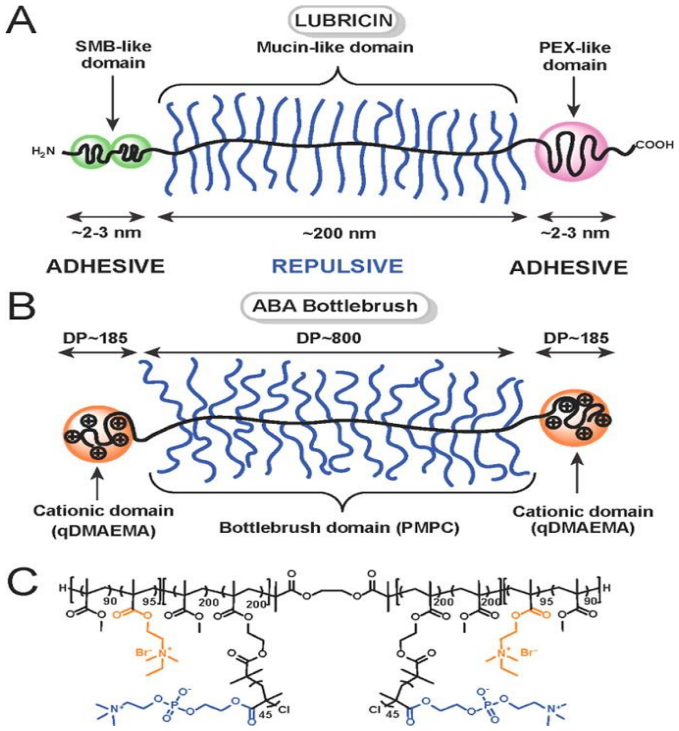

Figure 2. The structure of LUB. Image reproduced from Xavier Banquy et al [6].

Inspired by the unique structure of LUB, Yinqiang Xia et al. designed a highly stable, ultra-strong, fouling-resistant surface using triblock copolymers with bottle-brush structures of lubricin-like proteins [7]. The biomimetic bottle-brush polymer takes zwitterionic poly (2-methacryloyloxyethyl phosphorylcholine) (PMPC) as the main body of the polymer brush. Quaternized 2-(dimethylaminoethyl) methacrylate is the anchor end [6]. Through electrostatic interaction, hydrogen bond and other forces, it can be quickly and stably fixed on the surface of the substrate, forming an effective ring structure of the bottle-brush. The electro-neutral characteristic of phosphoriccholine effectively makes up for the deficiency of electrostatic adsorption and structural stability in the intermediate region of LUB (highly negative mucin) [8]. This structure shows ultra-strong antifouling performance in many kinds of protein systems and other systems. After evaluating with different techniques, it is found that this kind of polymers is 50 and 25 times more effective than LUB in reducing adsorption of serum albumin and lysozyme [8]. Also, it has almost no adsorption on complex systems such as simulated gastric juice, orange juice and milk, and has a strong antifouling ability.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

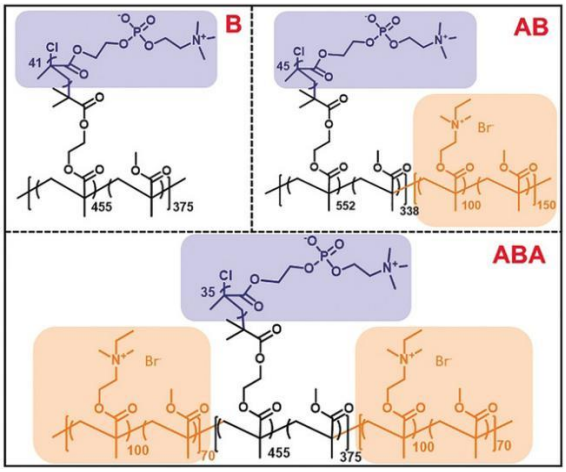

Figure 3. The molecular structures of bottle-brush polymer. The range part is the anchoring side groups, and the blue part is the pendant zwitterionic chains of the bottle-brush polymers. Image reproduced from Yinqiang Xia et al. [7]

It is worth mentioning that these biomimetic polymers can finish the modification of the substrate in 10 minutes only by a simple drop-casting or online exposure, which has low requirements on the substrate and strong stability. The surface of the polymer remains stable in a high salinity solution and under a wide pH range (2-8.5). Testing by the surface forces apparatus (SFA), it is found that it also has good stability under high pressure [7]. Therefore, the polymer not only has the convenience of graft-to modification but also has the stability of graft-from modification. The unique bottle-brush polymer structure provides strong steric repulsion force, which give the polymer efficient antifouling properties. More importantly, the strongly bound hydration layer on PMPC branches [8] also make the polymer present excellent antifouling performance. The biomimetic bottle-brush polymers are expected to be used for anti-pollution protection in prisms, optical fiber sensing and implanted medical devices.

3.2. Polypeptide

Protein absorption is typically the first step of bio-fouling progress which is a problem for many implant medical devices. Surface-grafted polymers present a decrease in conformational entropy contributing to large energetic barriers when proteins and bacteria are absorbed to the surface. Anti-biofouling strategies such as using self-assembled monolayers (SAM) and surface-grafted polymers synthesized by antifouling polymer brushes have been reported [9]. However, a problem is that these methods often need specific functional groups on the surface to bond with and the junction points between the substrate and grafted chains are vulnerable to hydrolysis or thermal degradation.

In order to avoid this problem, Messersmith et al. mimicked the structure of the mussel adhesive proteins (MAPs) which exist in the adhesive pads located at the end of byssal threads [10-12]. When mussels approach the substrates, they immediately eject proteinaceous liquid precursor secreted by glands in the mussels' foot. After rapidly hardening, the jets turn into collagen-like and silk-like proteins with exceptional strength. Scientists have pieces of evidence to convince that 3,4-dihydroxyphenylalanine (DOPA) [12], an uncommon residue in other proteins which is formed by posttranslational modification of tyrosine, is relevant to these adhesive interactions.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

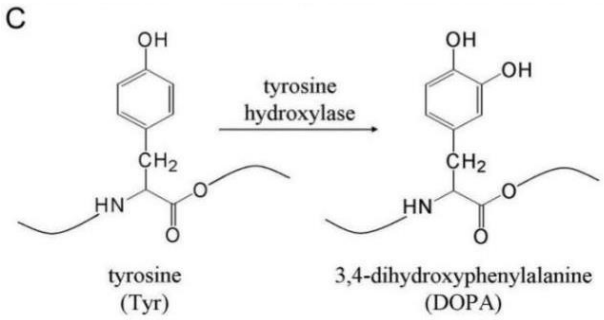

Figure 4. DOPA is produced by post-translational modification of Tyr. Image reproduced from Jeffrey L. Dalsin et al. [13]

The interesting thing is that antifouling surfaces can be designed using such an adhesive molecule. Messersmith and his fellows added an antifouling polymer chain [13] to the end of adhesive polypeptide and the surface fouling was changed because of the absorption of the polymer. There are two types of approaches to synthesize surfaces with antifouling materials: graft-to, in which polymer chain with adhesive end groups are synthesized and then attached to the surface; graft-from (graft-bottom), which means initiation groups are absorbed on the surface before the polymerization (Figure 5.).

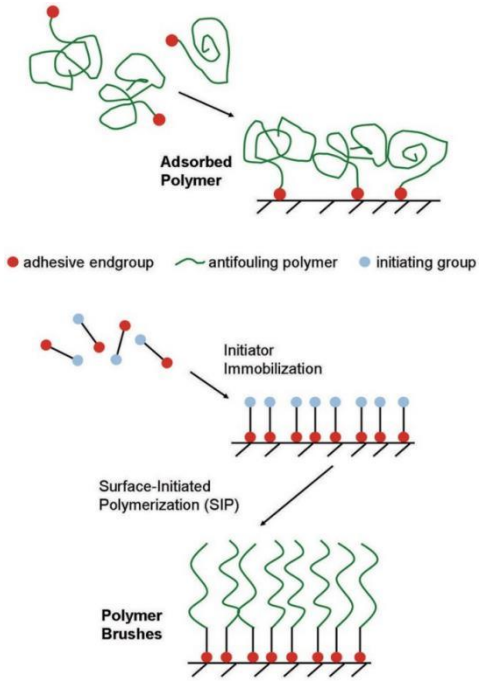

Figure 5. 'Graft-to' (top) and 'graft-from' (bottom) strategies for the modification of surfaces with antifouling polymers. Image reproduced from Jeffrey L. Dalsin et al. [13]

Jeffrey L. Dalsin et al. [13] conjugated Linear monomethoxy-terminated PEGs to a single DOPA residue (mPEG-DOPA) and the N-terminus of Ala-Lys-Pro-Ser-Tyr-Hyp-Hyp-Thr-DOPA-Lys (mPEG-MAPD) separately. Then they tested the cell attachment resisting ability of four surfaces respectively: mPEG-DOPA modified Ti surface, mPEG-DOPA modified Au surface, mPEG-MAPD-modified Ti surface and mPEG-MAPD-modified Au surface, after culturing 3T3 fibroblasts for up to 14 days. A reduction greater than 98% in the total projected cellular area has been reported when comparing the mPEG-MAPD 5k modified surface to unmodified gold. In order to design effective and long-lasting fouling resistant surfaces, Andrea R. Statz et al. designed

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

another kind of antifouling macromolecules composed of antifouling N-substituted glycine (peptoid) chains and biomimetic anchoring peptide. Peptoids eliminate backbone chirality and increase stability in a wide range of pH. Three types of peptidomimetic polymer (PMP1, PMP2, PMP3) were synthesized with the same biomimetic anchoring peptides and different anchoring peptoids (Figure 6.) [12]. Resistance to enzymatic degradation, protein adsorption, mammalian cell adhesion and bacterial cell attachment of TiO_2 substrates modified with PMP1, PMP2, or PMP3 were tested. The antifouling peptoid portions of the molecules were found resistant to enzymatic protease degradation (Figure 7.) [11], [12]. Also, a peptidomimetic polymer-modified TiO2 surface has been characterized using an experimental and theoretical method [14]. King Hang Aaron Lau et al. demonstrate that surface-grafted polysarcosine (PSAR) brushes whose side chains are more hydrophilic have a promising future for antifouling material because of its excellent resistance to cell and protein attachment [15].

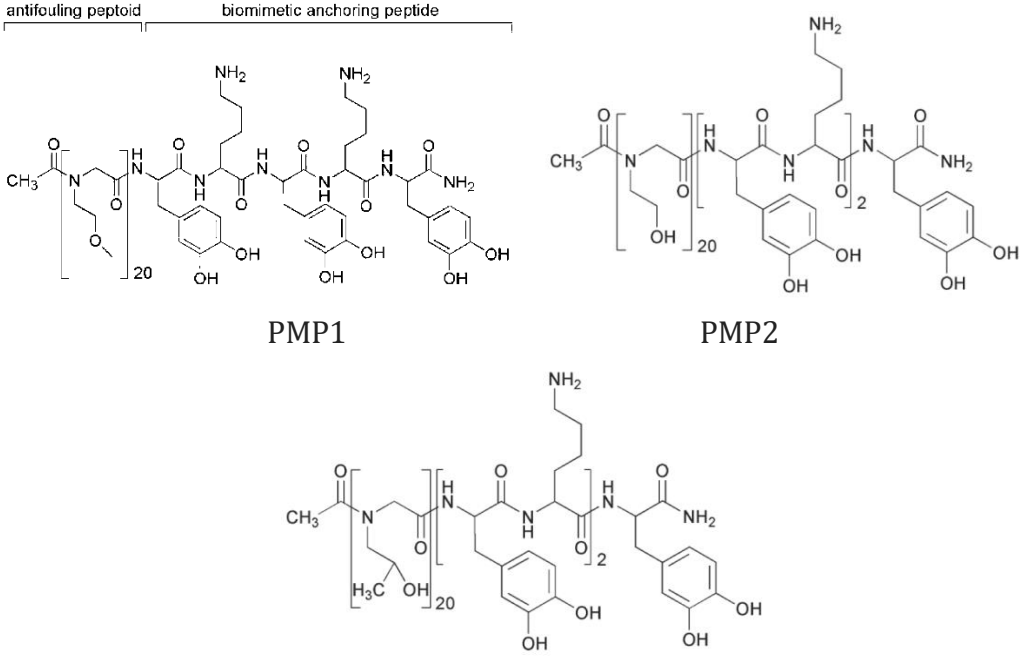

Figure 6. Chemical structures of PMP1, PMP2 and PMP3. [12]

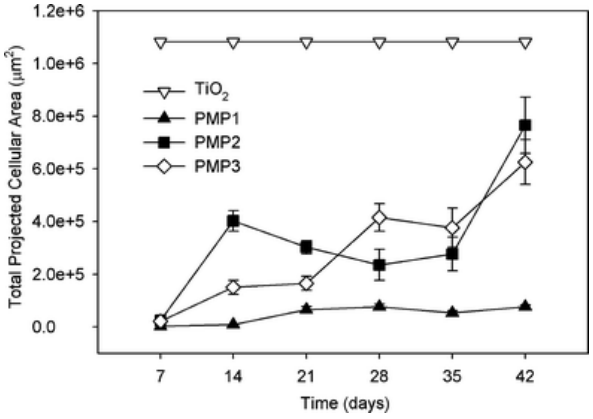

Figure 7. The total projected area of 3T3 fibroblasts during long-term cell-culture on unmodified TiO_2, PMP1-, PMP2-, and PMP3-modified TiO_2 substrates. Image reproduced from Statz, A. R. et al. [12]

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

When it comes to the graft-to approach, the initiation molecule usually contains a functional group that can easily attach to the surface physically or chemically and another functional group can conjugate antifouling polymer chain [10].

Not only non-ionic polymer chains but also functional polymer chains, like amphiphilic copolymers, zwitterionic polymers, polysaccharides and cationic polymers, can be attached to the biomimetic anchors to create diversified antifouling coatings [16]. Hyun Ok Ham et al. introduced a novel antifouling glycopeptide-mimetic polymer which contains an oligosaccharide side chain as an additional part of the former peptidomimetic polymer chain [17]. Results are attractive because the carbohydrate-rich glycocalyx they mimic has a high natural resistance of the glycocalyx toward nonspecific interactions.

They used M20Glu(OH) and M20Mal(OH) to modify TiO2 surface and investigated the resistant ability of the modified surfaces against fibrinogen adsorption (Figure 8.).

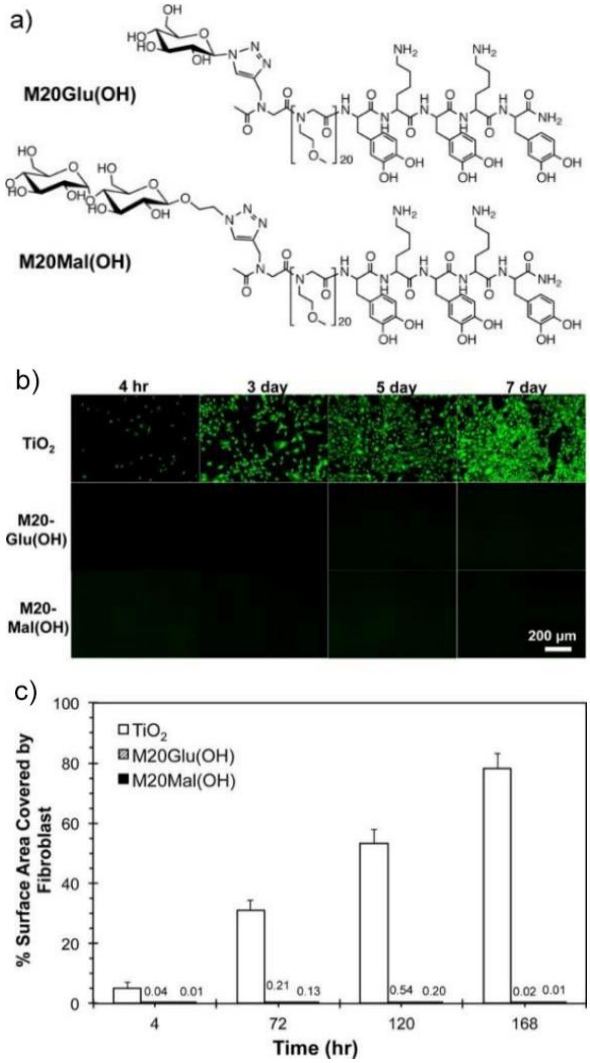

Figure 8. Chemical structures of M20Glu(OH) and M20Mal(OH) (a). Fibroblast adhesion on bare and glycopeptoid-modified TiO_2 substrates. Representative fluorescent images from each time point measured (b) and quantified % surface area covered by fibroblasts (c). Image reproduced from Hyun Ok Ham et al. [17]

The dopamine's molecular structure is so similar to DOPA that many researchers also pay attention to the polydopamine to pursue improvements of antifouling materials.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

3.3. Dopamine

The use of water purification technology is increasing rapidly both in private houses and industry. Because of the relatively low cost and high efficiency, membrane technology has become the most widely used method to purify or desalinate water. However, the problem of fouling of organic matter such as protein, oily wastewater emulsions and bacteria is damaging the membrane and this is the core problem of the whole technology because of the active attraction between the film surface and the foulant. As a result, people try to figure out how to reduce the favorable interaction between membrane and foulant to enhance membrane longevity and performance. There have been researches about surface modification techniques such as thin-film coatings [18], self-assembled monolayers [19], and chemical treatment grafted polymeric material (e.g., UV or plasma treatment) [20-22]. However, these techniques have some disadvantages. For example, the water permeability will decrease with the use of thin-film and self-assembled coatings. Another example is that the UV-grafting can only be used in membrane and it's hard and costly to apply plasma treatment in large-scale applications. What's more, these modifications can only be done before placing the membrane into the modules. Additionally, this technique cannot be used to deal with contamination of other wet film components such as spacers and the membrane module performance will be affected by the fouling of these components.

The use of bio-inspired techniques may solve these problems and allow the modification of films in irregular form. As it reported, dopamine can attach to multiple of substrate when it is oxidized by oxygen. With dopamine accumulating, the poly-dopamine (PD) layer formed. It is predicted that the PD imitates foot protain5 of Mytilus edulis (Mefp-5) by containing two chemical components: catechols and amines, which are widespread in Mefp-5. [23] Despite the fact that this chemical construction is under investigation, its microstructure is unclear yet.

It is acknowledged that the increase in facial hydrophilicity have associated with the increase in film fouling resistance. Accumulation of PD can render even highly hydrophobic surfaces hydrophilic. Therefore, it is speculated that this character may be useful in improving the fouling resistance of membrane surfaces [24]. What's more, PD film, the versatile immobilization platform, covalently fastens PEG to it surface [23]. Because of the 0.4-0.5 Flory–Huggins interaction parameter of PEG chains [25], the use of PEG chains to improve the hydrophilicity and bio-compatibility of membrane surfaces is prevalent [26]. It is predicted that the water molecules around PEG chains form a hydration shell, rendering PEG grafts able to repel contaminant [21].

It was reported 29 that by measuring the contact angle, analyzing emulsified oil fouling and determining the irreversible fouling, the PD-modified polyvinylidene fluoride (PVDF) microfiltration (MF) membranes showed a similar flux to the unmodified PVDF MF membranes (figure 9a.). The flux improved 1.5 times, and PD-g-PEG-modified PVDF MF membrane appear to reject the organic material at the same time. The most probable interpretation of flux grow in these MF membranes is that PD increased the wettability of the membrane leachy structure. The increasing deposition of organic matter on the PD-film lead to a reduction of pore size. When the pores are reduced to a negligible size, PD makes more pores moist, which increase the flux of the whole film [27].

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

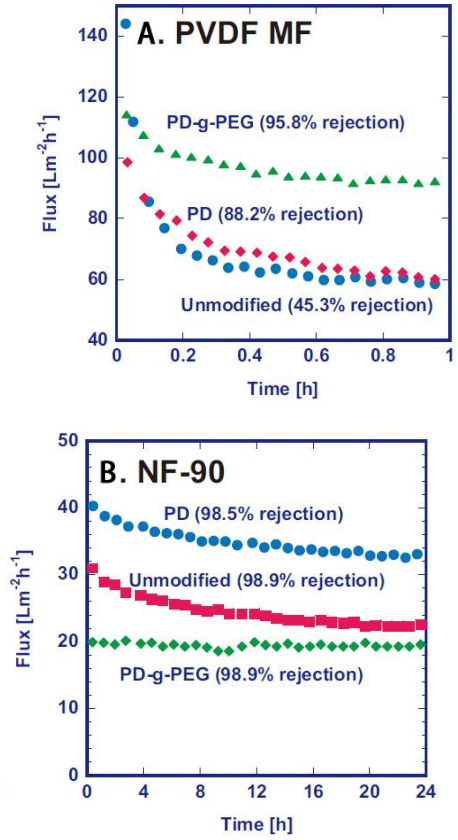

Figure 9. Oily water fouling behavior of flat membranes. The change of film flux of oil emulsion with time. The material respectively used unmodified, PD-modified, and PD-g-PEG-modified (a) PVDF MF and (b) NF-90 membranes. (a) reports the ability to repel Organism, (b) reports the ability to repel Nal. (i.e., t = 1 h for(a), t = 24 h for (b)). Image reported from Bryan D. McCloskey et.al. [16]

The high mass transfer resistance caused by PEG grafting leads to a low flux of PD-G-PEG films. The low flux did not change with time suggests good fouling resistance (figure 9b.). Therefore, for the nanofiltration (NF) membranes, PD modification improves the fouling results and there is no fouling in the membrane after PD-g-PEG modification.

As a result, the organic-resistant ability of most of modified MF and ultrafiltration (UF) films are stronger than their unmodified copies. So, PD-based membrane modifications provide an optimistic prospect for development to improve the antifouling capability of the film in large-scale water purification equipments.

4. ANTIFOULING SURFACES INSPIRED BY NATURAL MEMBRANES

In recent years, membrane technology has attracted more and more attention and been widely used. This section involves two significant applications of membrane technologies: membrane filtration and antifouling coatings. Two kinds of membranes/films will be introduced. One is the thin-film nanofiltration membrane containing zwitterionic polyelectrolyte nanoparticles (TFN-ZPNP) and the other is the nacre-inspired mineralized (NIM) film. Their developers drew inspirations from aquaporin and nacre respectively and these films have very specific properties due to their similar micro/nanostructures to natural surface membranes'. However, to solve different issues in diverse fields, principles utilized vary because of the different demands of the surface materials. There is no doubt that both of these two kinds of films have made improvements that cannot be ignored.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

4.1. Aquaporins

As one of the most significant separation methods, membrane technology is applied in various fields such as industrial wastewater treatment and biomedical substance separation [28]. With the higher market demands for existing membranes, proving filtration efficiency becomes the main challenge. For filtration efficiency, the two most valuable properties are permeability and selectivity, but they are often regarded to be inversely proportional to each other [29] [30]. The biological membranes, however, exhibit both of these two properties outstandingly because the lipid bilayer of them contains transmembrane protein channels [31], [32]. Among these channels, researchers have studied the water channel membrane proteins, aquaporins (APQs) for their special water transport capability which can reach 3×10^9 water molecules per subunit per second. This capability is gained from their unique construction of nanochannels, inferring the importance of the roles played by nanochannels in the fields of nanofiltration membranes featuring selectivity, permeability and antifouling properties during the process of clean water production and purification.

In 2016, Yan-Li Ji et al. have published a paper about TFN-ZPNP standing for thin-film nanocomposite (TFN) membrane containing zwitterionic polyelectrolyte nanoparticles (ZPNPs), managing to prepare a brand-new nanofiltration membrane with unprecedented performance for water treatment. Inspired by “water channel” structures of APQs, the core technology of this membrane is to create interfacial space as water channels between the polyamide matrix and dispersed ZPNPs to improve its water permeability and solute selectivity. Therefore, the most ingenious part of this experiment is the synthesis of a novel kind of ZPNPs of excellent properties, which determines the beneficial chemical structures (shown in Figure 11.) and the successful formation of the channel and is the basis of the entire material. Yan-Li Ji et al. introduce the first synthesized ZPNPs containing zwitterionic sulfobetaine groups into their nanofilms, which can reduce the roughness while increasing the surface hydrophilicity, electronegativity. They got the inspiration by the existence of zwitterionic phospholipids at the outside lipid layer of cell membranes, which endows well-known extra good fouling resistance. Hence, this novel kind of films also has good antifouling properties.

In the study of Yan et al., what is clever is that they synthesized a kind of ZPNP containing sulfobetaine groups. After that, TFN-ZPNP membranes were made on supporting polysulfone ultrafiltration (PSF-UF) membranes in which the particles and PIPs chemically cross-linked with TMC to form the polyamide matrix containing ZPNPs. They also prepared pristine TFC membranes without ZPNPs for comparison [33].

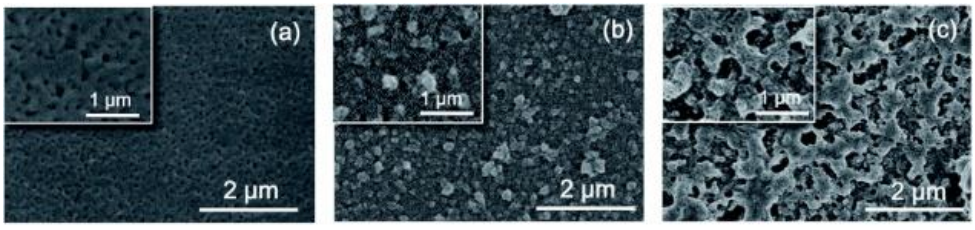

Figure 10. FESEM surface morphologies of (a) PSF-UF, (b) TFC, and (c) TFN-ZPNP membranes. Image reproduced from Yan-Li Ji et al. [33]

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

Figure 11. Schematic illustration of the microstructure and separation performance of the TFN-ZPNP membrane. Image reproduced from Yan-Li Ji et al. [33]

Holding the theme of this article, we will focus on the causes of antifouling resistance next. Antifouling property is an important index that is required in the applications of separation membranes in water treatment. In this experiment, the TFN-ZPNP membrane was tested with the model foulant, bovine serum albumin (BSA) and it demonstrated its good antifouling ability (Figure 14.). First, the relatively smooth and loose hydration layer formed by sulfobetaine groups on interfacial channel makes the attachment of protein difficult. Analyzed by FESEM, a 200-300nm selective layer was found on the porous PSF-UF support for both membranes with or without ZPNPs. However, when ZPNPs were added, membrane surfaces became much smoother and looser (Figure 10.). The formation of this morphology is probably because the firm fixing of polyamide macromolecules on ZPNPs [34] is prevented by the water molecules around Sulfobetaine groups of ZPNPs. Thus, the interfacial space is produced (Figure 11.). Besides, the partially enclosure of Sulfobetaine groups leads to the decrease in the rate of interfacial polymerization reaction; so, both ZPNPs and polyamide macromolecules could arrange regularly and form a relatively smooth and loose membrane surface.

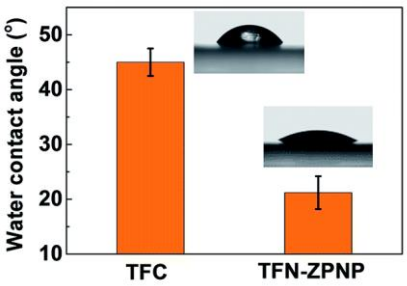

Figure 12. The water contact angle of TFC and TFN-ZPNP membranes. Image reproduced from Yan-Li Ji et al. [33]

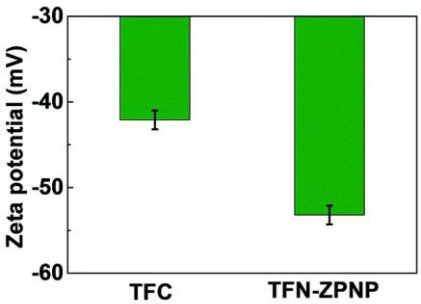

Figure 13. Zeta potential of TFC and TFN-ZPNP membranes. Image reproduced from Yan-Li Ji et al. [33]

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

Second, the enhanced hydrophilicity delivered by ZPNPs weakens the membrane surface's attractive force to the hydrophobic BSA molecules. For the reason of the hydrophilicity of Sulfobetaine groups in ZPNPs, the hydrophilicity of the as-prepared TNF-ZPNP membranes were also strengthened. As shown in Figure 12, the water contact angle decreases from 45 degrees to 20 degrees after the introduction of ZPNPs, indicating the better hydrophilicity of the TFN-ZPNP membrane. In addition, due to the existence of ZPNPs, the increased miscibility between organic and aqueous solutions enhances the hydrophilicity, because more carboxylic acid groups were created by the hydrolysis of acryl chloride groups of TMC. As a result, the TFN-ZPNP membrane becomes more hydrophilic and more electronegative (as shown in Figure 13. by the reduced zeta potential).

Third, antifouling performance usually can be controlled by surface charge and as mentioned in last paragraph, TFN-ZPNP membrane is negatively charged, bringing an electrostatic repulsive interaction between the BSA molecules (PI=4.7) and membrane surface, which maintains a certain distance between the two. Thus, the membrane gain a good antifouling performance.

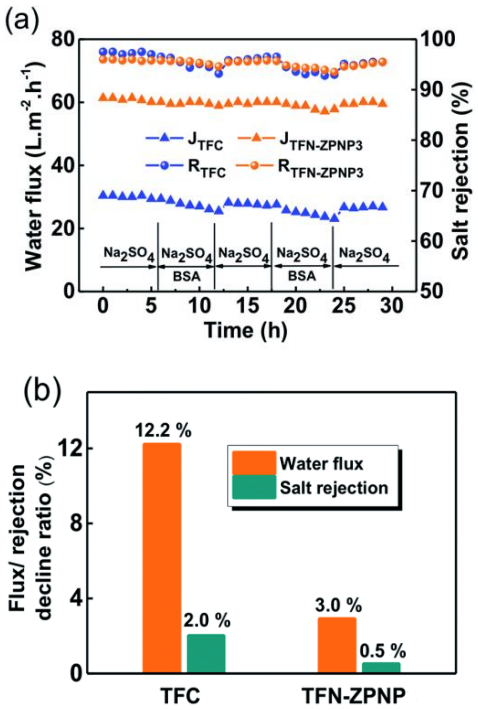

Figure 14. Antifouling performance: (a) water flux and salt rejection vary with operation time; (b) final water flux and salt rejection decline ratio of TFC and TFN-ZPNP membranes tested with 1 g L^{-1} aqueous Na_2SO_4 and 1 g L^{-1} aqueous Na_2SO_4 + 0.1 g L^{-1} bovine serum albumin (BSA) solution, pH = 7.0 at 25 °C and 0.6 MPa. Image reproduced from Yan-Li Ji et al. [33]

4.2. Mineralized Film

As marine environmental issues, especially oil spills, occur more frequently, the demand for underwater superoleophobic materials gradually becomes urgent, ensuring their broad applications in various fields [35-37]. The basic elements to make underwater superoleophobic materials are high surface energy and hierarchical micro/nanostructures to make surfaces superhydrophilic in air. These materials then can trap water molecules as cushion to repel oil droplets [38-41]. However, due to these hierarchical micro/nanostructures, non-transparent coatings can be rendered as a result of broad light scattering effect. This significantly blocks these coatings' applications in underwater optical devices and equipment such as underwater

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

cameras and swimming goggles. Besides, most of these materials are vulnerable due to poor mechanical strength, for they will lose superoleophobicity under severe marine conditions in a short time [42], [43]. Though in previous works, different kinds of hydrogels [42], [44-46] have been utilized successfully to fabricate coatings with mechanically robust underwater superoleophobicity. Unfortunately, mechanical properties and transparency are usually mutually exclusive. In general, the inventions of an advanced underwater superoleophobic coatings featuring not only mechanical robustness but also high transparency remained blank until recently.

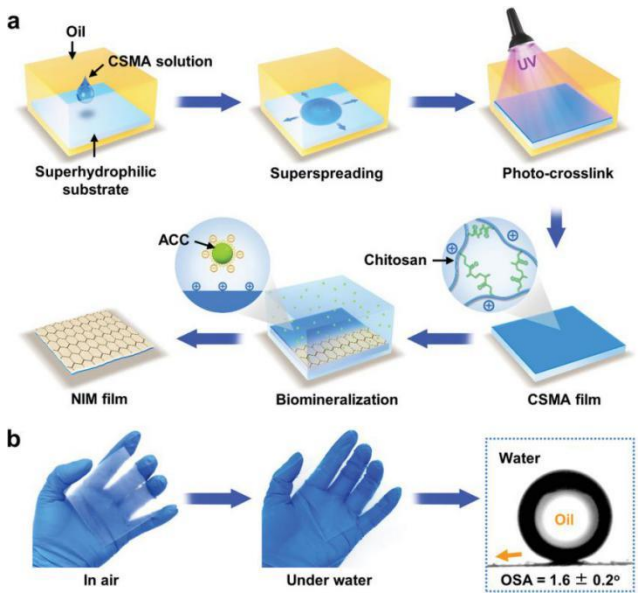

Figure 15. Design and fabrication of nacre-inspired mineralized (NIM) film with high transparency and superoleophobicity underwater. Image reproduced from Wei Chen et al. [42]

Lately, inspired by natural nacre, Chen et al. developed NIM film, standing for the nacre-inspired mineralized film and filled the blank. What makes nacre so special is that its internal soft body is well protected attributed to the excellent mechanical performance which greatly relies on the hierarchical organization induced by biomineralization of approximately 5% organic framework and 95% inorganic aragonite component [47], [48]. Thus, the film of natural nacre is both stably underwater superhydrophobic and highly transparent. To mimic it, Chen et al. combined the superspreading and biomineralization strategies (Figure 15a) and presented the NIM films which are not only given high transparency but display an ultralow oil adhesion (Figure 15b) and mechanically robust underwater superoleophobicity [45].

For the inorganic component of the NIM film, they chose aragonite platelets and for the organic component, they chose CSMA. The prepared NIM films and nacre films are very similar in chemical composition and micro/nanostructure which leads to prominent Voronoi patterns (Figure 16.) [49-50]. Thus, they completed a perfect imitation and it is not difficult to conclude that this novel kind of films will act as superior as the nacre films.

First, the NIM shows a stable oil-repellent property towards various oils, including engine oil, silicone oil, mineral oil and cyclohexane. Even under high external pressure, the adhesive forces of the films to oil are very low. It can tolerate a preload more than 100 μN when most other superoleophobic underwater materials can only stand 40 μN.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

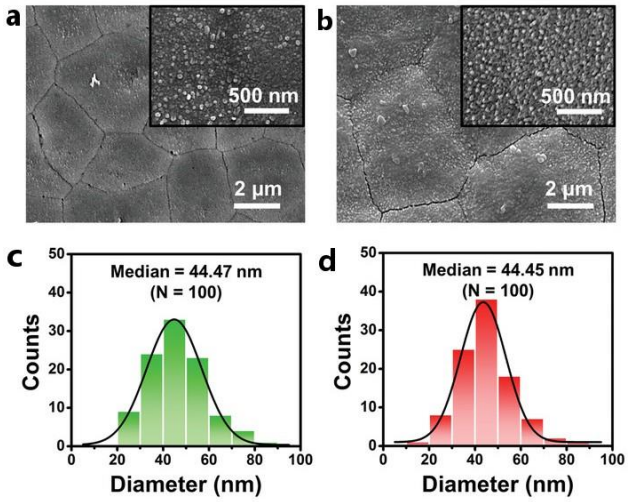

Figure 16. The NIM films are similar to natural nacre in chemical composition and physical structures. a,b) Surface hierarchical micro/nanostructures of nacre and NIM films. c,d) Diameter distribution of nanograins on the film surfaces calculated from the inset images in (a) and (b). Image reproduced from Wei Chen et al.[42]

Besides, the underwater superoleophobicity of NIM films is not sensitive to high salinity. NIM films exhibit both ultralow oil adhesion and superoleophobicity in water with a range of NaCl solutions with concentrations ranging from 0 to saturation. This indicates that it has excellent oil repellency regardless of high ionic strength and salinity. NIM film can maintain its original micro/nanostructure, superoleophobic and ultralow adhesion even after soaking in artificial seawater for 30 days. As a result, the NIM film has strong oil repellency and can be put to practical use in the marine environment. What's more, the nacre-like characteristics endow the NIM film with excellent mechanical properties, resulting in a mechanically strong underwater superoleophobicity. Therefore, the NIM films has durable superoleophobicity, even after suffering crude treatments such as sand grain impingement, which is important for underwater oil-repellent materials.

5. ANTIFOULING SURFACES INSPIRED BY NATURAL SURFACES

Scientists are good at discovering not only the molecular mechanisms inside organisms but also the special structures and patterns of the surfaces of animals and plants. In this part, we introduce several surfaces whose specific fouling resistance attributes to their distinctive structures rather than antifouling biomolecules. Therefore, various materials and methods are applied to mimic these patterns. Polymer materials such as PEG and PMMA are basic materials to replicate the structure because of their good machinability. Then, researchers apply other materials such as metals and alloys to imitate the nature surfaces instead of strict duplication and materials with their intrinsic functions will improve the surface character.

5.1. Butterfly Wings and Rice Leaf

The microstructure of shark skin inspires the "antifouling and low resistance" surface, and the design of "self-cleaning" coating is inspired by the engineering technology of hydrophobicity and low adhesion of lotus leaf. Rice leaf and butterfly wings combine the ideal shark skin and lotus leaf effect.

Figure 17a. shows the hierarchical configuration of rice leaves. For rice leaves and butterfly wings, the horizontal grooves with a horizontal sinusoidal pattern in rice leaves and orderly tile scales in butterfly wings contribute to the anisotropic flow. Figure 17b. shows a general model

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

of the layered structures. A sinusoidal pattern of micropapillae with height 2–4 μm, diameter 2–4 μm, pitch 5–10 μm, and peak radius 0.5–1 μm cover the rice leaf surfaces [49]. The water droplets can improve self-cleaning efficiency by rolling and take away particles on the rice leaf surfaces [50].

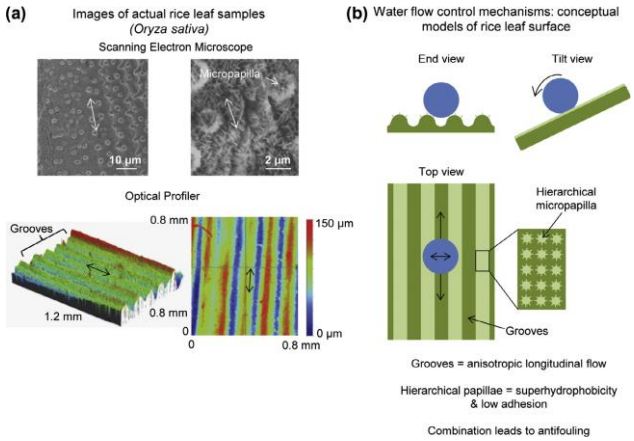

Figure 17. Optical profiler height images of (a) actual rice leaf and (b) a conceptual model of water flow control mechanisms (adapted from Bixler and Bhushan [52]). Arrows indicate trends in horizontal and vertical flow. Image reproduced from Gregory D.Bixler et.al.[4]

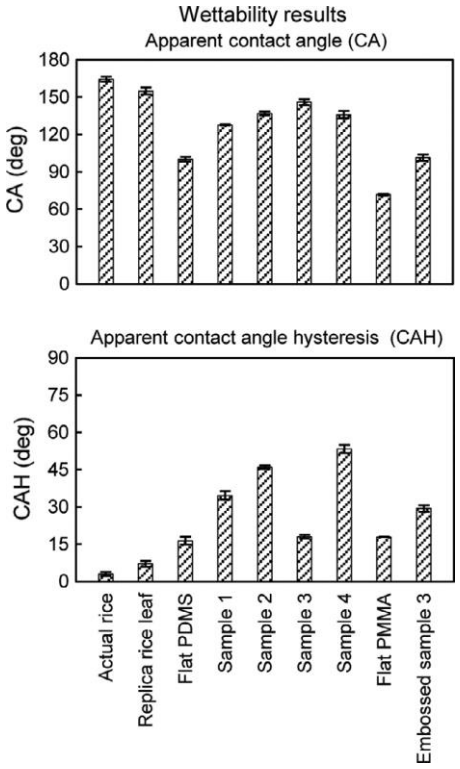

Figure 18. The results of CA and CAH experiments [50]. The experiment samples include actual rice leaf, rice leaf replica (with superhydrophobic nanostructured coating), flat PDMS and PMMA, Samples 1–4, and Embossed sample 3. The result shows that high CA and low CAH can improve the self-cleaning efficiency. Image reproduced from Gregory D.Bixler et.al.[4]

Embossing a flexible glue-backed polymer film can create effective and cheep antifouling surfaces. Hot embossing can be done by heating the main die and pressing into the polymer film and it this method can be used to modify irregular surfaces. The technique depends on the type

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

of the main die and the forming material (i.e. composition, thickness, characteristic size). The main die is usually made of silicon or metal. It has been shown that embossing can produce various structures with submicron scale characteristics.

Experimental materials of polyurethane soft lithography, PDMS soft lithography and hot-embossing process production, respectively for its anti-biofouling, anti-inorganic and wettability were measured. The experiment chose the E.coli as the foulant to measure anti-biofouling ability. Self-cleaning experiments were conducted to measure anti-inorganic fouling ability. To test wettability, apparent contact angle (CA) and contact angle hysteresis (CAH) were measured in different samples. Sample 1 has hexagonal array of single height pillars with an average height of 2μm. Sample 2 is 2μm height. Sample 3 has commutative rows of dual height pillars height 2μm, 4μm. Sample 4 has commutative lines of single height pillars with average high of 2μm and ribs with average height of 4μm.

Anti-biofouling experiment shows that microorganisms are difficult to adhere to surfaces in flowing liquid. Figure 18. suggests the CA and CAH measured in different samples. Actual rice leaves and butterfly wings shows similar result to the self-cleaning experiment that the high CA and low CAH samples can prevent inorganic fouling most efficiently and improve the efficiency of fouling-resistant nanostructure coating samples which showed low adhesive force. Natural rice leaf has the biggest CA at 164° and the smallest CAH at 3° which indicate that it can resistant water easily on its surface [50]. Compared with uncoated samples, nanostructured coated samples were easier to remove particles, and the CA of Cassie-Baxter wet hydrophobic rice leaf replication sample was higher than that of uncoated samples, demonstrating the effectiveness of superhydrophobic coating.

5.2. Shark Skin

Shark skin is a typical structure that has been mimicked because of its special pattern as well as drag-reducing and antifouling function [51], [52]. From the SEM and CLSM images of different location of the shark (Figure 19.) [53], we can see though slight variances of the scales still exist, the dermal denticles shaped like small riblets are aligned in the direction of fluid flow. Some explanations have been reported to explain the biofouling resistance ability of shark skin: (a) The fast-flowing water can inhibit small marine organisms attaching on the skin and wash those organisms that have already settled. (b) The epidermal cells provide a mucosal coating that works as a barrier between the surface and external factors. (c) The length scale of the shark skin's surface texture is smaller than the fouling organisms, so the microtopography deters the settlement.

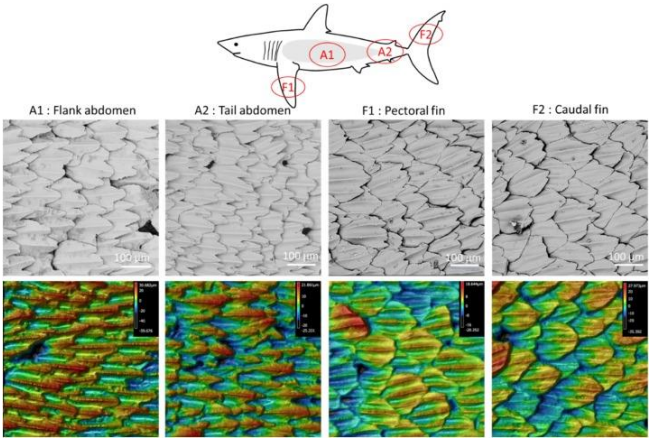

Figure 19. SEM (upper) and CLSM (lower) images of the Mako shark skin surface at different body locations. Image reproduced from Hsiu-Wen Chien et al.[53]

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

Hsiu-Wen Chien et al. replicated the pattern of the tail abdomen (A2) and pectoral (F1) with PMMA and then tested its bacterial resistance using S. aureus and E. coli. The results of the amounts of biofilm formed on the surfaces after 1,7 and 14 days, measured by crystal-violet staining indicated that the physical structure of shark skin surface can reduce microorganism attachment. (Figure 20.)

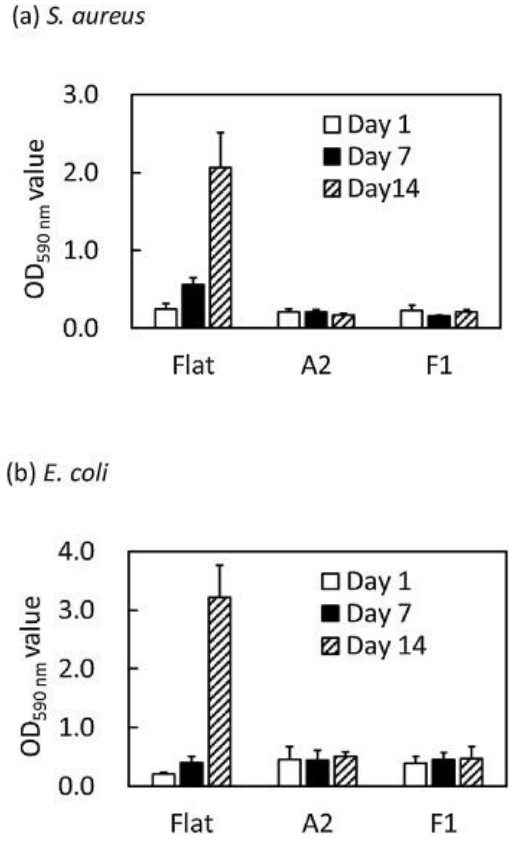

Figure 20. The residual biofilms of (a) S. aureus and (b) E. coli were quantified bycrystal-violet staining. Image reproduced from Hsiu-Wen Chien et al. [53]

"Sharklet AFTM" is a kind of pattern inspired by shark skin created by Anthony B. Brennan et al. [54] The topography of 'Sharklet AFTM' consists of a highly ordered series of bars and pillar features, which do not closely match the structures on shark skin. This pattern is originally made of silicon using photolithography technology, which exhibits effective inhibition of bacteria.

Arisoy et al. [55] combined antibacterial titanium dioxide (TiO_2) nanoparticles (NPs) with shark skin patterns because TiO_2 can react with H_2O or OH- after absorbing the UV light and produce active radicals or ions which can destroy the outer membrane of bacteria. Solvent-assisted nanoimprint lithography (NIL) technology is used to fabricate the orthogonal surfaces on poly(ethylene terephthalate) (PET) substrates. Norland Optical Adhesive 60 (NOA), TiO_2-10 (10 wt %TiO_2/90 wt %NOA), TiO_2-50 (50 wt %TiO2/50 wt %NOA) and TiO_2-C (90 wt %TiO_2/10 wt % tetraethyl orthosilicate) were spin-coated onto PET substrates. Bacteria resistant ability of different composites was tested using E. coli as the influence factor (Figure 21.) and results showed that TiO_2-made shark skin mimic surface could reduce the attachment of E. coli by 70% ~ 85%.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

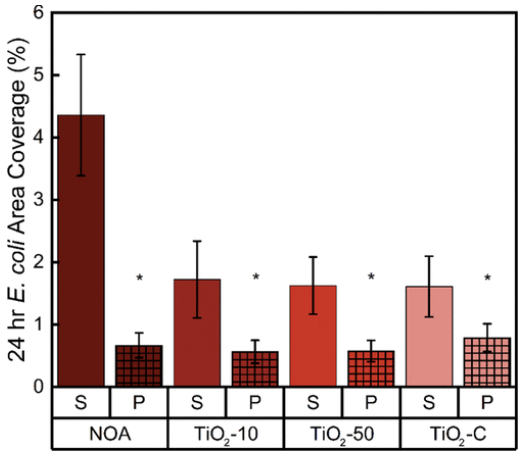

Figure 21. 24 h area coverage of surface-adhered E. coli on smooth films (S) versus patterned surfaces (P) of NOA, TiO_2 -10, TiO_2-50, and TiO_2–C. An asterisk (*) denotes 95% significance between smooth and patterned samples. Error bars denote standard error. Image reproduced from Arisoy et al. [55]

5.3. Earthworm

Earthworms often crawl out of the mud nakedly, without bringing a grain of earth on their body. They also shuttle under the hard ground, without causing even a little damage. These simple natural phenomena actually reveal the unique lubrication and anti-fouling properties of earthworms. This characteristic is closely related to the strong secretory system and concave and convex body surface structure of earthworm. A strong secretory system allows earthworms to secrete a large amount of mucus in a short time, and the concave and convex body surface structure helps to wrap this mucus, thus forming a thick slippery layer (Figure 22.) [56] between the surface of the earthworm and the soil particles, preventing direct contact between the soil and the earthworm skin, achieving antifouling and self-cleaning effect. It is important to point out that in the process of movement, the intense physical friction of the solid will carry away part of the mucus, but the earthworm can always recognize this loss, timely replenish the mucus to maintain the slimy characteristics.

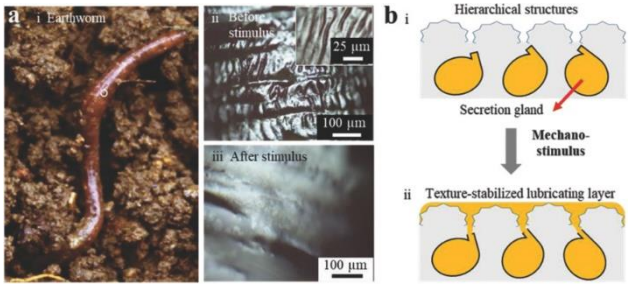

Figure 22. Earthworm prototype. a) Images of an alive earthworm moving out from moist soil (i); image of earthworm's skin before (ii) and after stimulus (iii); b) Schematic for surface texture and secretion mechanism. Image reproduced from Huaixia Zhao et al. [56]

The team of Huaixia Zhao et al. has made some progress in mimicking the self-lubricating mechanism of earthworms. In the early stage, they developed a kind of gel material with the property of self-modulated secretion [57], [58]. This material can wrap the silicone lubricant in the urea and polydimethylsiloxane copolymer (uPDMS) supramolecular polymer matrix. After the loss of surface silicone lubricant, silicone oil can be released automatically. Using a simple and efficient method called "Breath figures" [59], they prepared texturing structures of a certain size on the surface of such materials, thus producing a self-lubricating coating that is similar to

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

earthworms. In simple terms, they first prepared tetrahydrofuran (THF) solution containing uPDMS and silicone oil and then applied this solution to the substrate. In high humidity, the evaporation of solvent THF induces condensation of moisture in the air on the surface of the polymer concentrated solution [60]. As the preparation process progresses, the condensate droplets will further evaporate, leaving behind surface texturing structures of a certain size (Figure 23a). The uPDMS supramolecular polymer gels are formed by the crosslinking of hydrogen bonds with dynamic reversibility. Thus, when it is disturbed by external mechanical forces, the crosslinking equilibrium will move rapidly so that the entrapped liquid can be released quickly. These released lubricants are held in place by the textured surface and then form a thick layer of lubrication (Figure 23b).

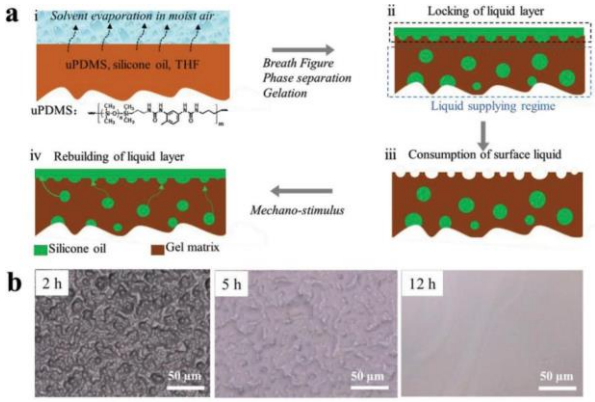

Figure 23. (a) The fabrication and liquid-release process of gel films. (b) Top-view image of a gel film being forming at different times. Image reproduced from Huaixia Zhao et al. [61]

The research team illustrated the anti-fouling property of this earthworm-inspired (EWI) film. Soil with different moisture was selected to simulate earthworm's living environment. Firstly, four samples were putting into the mud with 40% moisture. After a period of time, serious contamination was observed on flat and rough uPDMS films. However, the samples with flat uPDMS-150% oil film and EWI film maintained relatively clean surface (Figure 24.) and this is due to the slippery hydrophobic lubricating layer on their surfaces. In a high moisture environment, a water/oil interface between soil and the film could be induced and then the moist soil (pollution) could be removed easily. Secondly, when the soil moisture decreased to 20%, pollution on the flat uPDMS-150% oil film increased rapidly while the EWI film still kept a clean surface, which is also due to the unique earthworm-inspired structure. On the textured surface of EWI film, a thick oil layer formed and was fixed by the texture. As the film was dragged across the soil, the oil released mixed with the soil in contact, forming an intermediate layer between the oil layer and the soil layer. In the interface between the oil layer and the soil-oil intermediate layer, interface slip occurs under the action of physical shear, resulting in the removal of soil and some oil [60]. However, under the same condition, on the flat uPDMS-150% oil film, it was not able to form such a soil-oil intermediate layer to protect the film. In the dried soil powder condition, the mechanism is the same. In this case, there is no doubt to say that among above films, only the earthworm-inspired film has the ability to hold excellent antifouling property.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

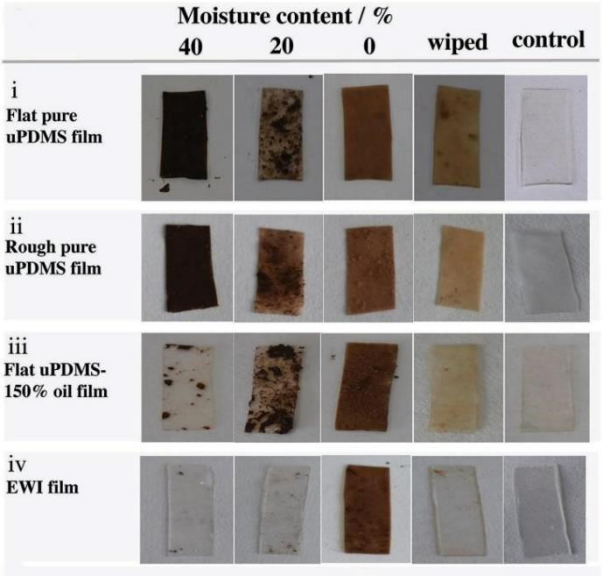

Figure 24. Antifouling property of the uPDMS materials under different soil conditions. Image reproduced from Huaixia Zhao et al. [61]

To sum up, inspired by the texture surface morphology and the unique adaptive secretion system of earthworms, a kind of soft polymer antifouling coatings used in solid-based environments is proposed and developed. The coatings have an oil slippery layer locked by surface's texture. When this slippery layer on the material surface is lost under the external influence, it can be regenerated at any time under the stimulation of external mechanical forces, so as to realize the sustainable use of this material. Therefore, the earthworm-inspired lubrication mechanism is conducive to the design and development of friction-reduction, self-cleaning and antifouling coatings used in solid environments.

6. SUMMARY AND FUTURE PERSPECTIVES

In this review, we summarize several effective strategies inspired by nature to ease the fouling problems. These strategies are classified by which structure they are inspired from. Lubricin, polypeptides and dopamine exhibit a specific structure that contains a sticky anchoring domain and a hydrophilic antifouling chain. By studying the characteristics of natural membranes in nature, such as nacre films and cell membranes, artificial membranes and membrane technologies have developed very well and have good prospects. Surfaces inspired by animal skin or plants' surfaces show that researchers can control the fouling resistance by adjusting patters of surfaces.

However, challenges still exist. These include: improving the durability of antifouling materials in various situations including in vivo conditions and natural environment; improving versatility to enable a certain pattern adaptable to various conditions; enhancing fouling resistance ability by discovering other nature structures.

Surfaces inspired by nature provide us broad ways of creating antifouling surfaces. We are looking forward to new strategies inspired by a novel structure and improvement in the existing models.

ACKNOWLEDGMENTS

The authors acknowledge the support of Anish Tuteja, Associate Professor of Materials Science and Engineering, Macromolecular Science and Engineering and Chemical Engineering,

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI. The authors' names are arranged in alphabetical order of the last names for their equal contribution.

REFERENCES

[1] Damodaran, V. B.; Murthy, N. S., Bio-inspired strategies for designing antifouling biomaterials. Biomaterials research 2016, 20, 18-18.

[2] Bixler, G. D.; Bhushan, B., Biofouling: lessons from nature. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 2012, 370 (1967), 2381-2417.

[3] Bhushan, B., Biomimetics: lessons from nature - an overview. Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences 2009, 367 (1893), 1445-1486.

[4] Bixler, G. D.; Theiss, A.; Bhushan, B.; Lee, S. C., Anti-fouling properties of microstructured surfaces bio-inspired by rice leaves and butterfly wings. Journal of Colloid and Interface Science 2014, 419, 114-133.

[5] Bhushan, B.; Jung, Y. C., Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction. Progress in Materials Science 2011, 56 (1), 1-108.

[6] Banquy, X.; Burdyńska, J.; Lee, D. W.; Matyjaszewski, K.; Israelachvili, J., Bioinspired Bottle-Brush Polymer Exhibits Low Friction and Amontons-like Behavior. Journal of the American Chemical Society 2014, 136 (17), 6199-6202.

[7] Xia, Y.; Adibnia, V.; Huang, R.; Murschel, F.; Faivre, J.; Xie, G.; Olszewski, M.; De Crescenzo, G.; Qi, W.; He, Z.; Su, R.; Matyjaszewski, K.; Banquy, X., Biomimetic Bottlebrush Polymer Coatings for Fabrication of Ultralow Fouling Surfaces. Angew Chem Int Ed Engl 2019, 58 (5), 1308-1314.

[8] Chen, S.; Zheng, J.; Li, L.; Jiang, S., Strong Resistance of Phosphorylcholine Self-Assembled Monolayers to Protein Adsorption: Insights into Nonfouling Properties of Zwitterionic Materials. Journal of the American Chemical Society 2005, 127 (41), 14473-14478.

[9] Prime, K. L.; Whitesides, G. M., Adsorption of proteins onto surfaces containing end-attached oligo(ethylene oxide): a model system using self-assembled monolayers. Journal of the American Chemical Society 1993, 115 (23), 10714-10721.

[10] Messersmith, J. L. D. a. P. B., Bio-inspired antifouling polymers. 2005.

[11] Statz, A. R.; Meagher, R. J.; Barron, A. E.; Messersmith, P. B., New Peptidomimetic Polymers for Antifouling Surfaces. Journal of the American Chemical Society 2005, 127 (22), 7972-7973.

[12] Statz, A. R.; Barron, A. E.; Messersmith, P. B., Protein, cell and bacterial fouling resistance of polypeptoid-modified surfaces: effect of side-chain chemistry. Soft Matter 2008, 4 (1), 131-139.

[13] Jeffrey L. Dalsin, B.-H. H., Bruce P. Lee, and Phillip B. Messersmith*, Mussel Adhesive Protein Mimetic Polymers for the Preparation of Nonfouling Surfaces. J. AM. CHEM. SOC 2003.

[14] K. H. Aaron Lau, C. R., Sung Hyun Park, Igal Szleifer, and Phillip B. Messersmith, An Experimental Theoretical Analysis of Protein Adsorption on Peptidomimetic Polymer Brushes. Langmuir 2011, (Bioinspired Assemblies and Interfaces).

[15] Lau, K. H.; Ren, C.; Sileika, T. S.; Park, S. H.; Szleifer, I.; Messersmith, P. B., Surface-grafted polysarcosine as a peptoid antifouling polymer brush. Langmuir 2012, 28 (46), 16099-107.

[16] Xu, L. Q.; Neoh, K.-G.; Kang, E.-T., Biomimetic Anchors for Antifouling and Antibacterial Polymeric Coatings. In Reversible Deactivation Radical Polymerization: Materials and Applications, American Chemical Society: 2018; Vol. 1285, pp 233-261.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

[17] Ham, H. O.; Park, S. H.; Kurutz, J. W.; Szleifer, I. G.; Messersmith, P. B., Antifouling Glycocalyx-Mimetic Peptoids. Journal of the American Chemical Society 2013, 135 (35), 13015-13022.

[18] Sagle, A. C.; Van Wagner, E. M.; Ju, H.; McCloskey, B. D.; Freeman, B. D.; Sharma, M. M., PEG-coated reverse osmosis membranes: Desalination properties and fouling resistance. Journal of Membrane Science 2009, 340 (1), 92-108.

[19] Luo, M. L.; Zhao, J. Q.; Tang, W.; Pu, C. S., Hydrophilic modification of poly(ether sulfone) ultrafiltration membrane surface by self-assembly of TiO2 nanoparticles. Applied Surface Science 2005, 249 (1-4), 76-84.

[20] Revanur, R.; McCloskey, B.; Breitenkamp, K.; Freeman, B. D.; Emrick, T., Reactive Amphiphilic Graft Copolymer Coatings Applied to Poly(vinylidene fluoride) Ultrafiltration Membranes. Macromolecules 2007, 40 (10), 3624-3630.

[21] Ulbricht, M.; Belfort, G., Surface modification of ultrafiltration membranes by low temperature plasma .2. Graft polymerization onto polyacrylonitrile and polysulfone. Journal of Membrane Science 1996, 111 (2), 193-215.

[22] Ulbricht, M.; Matuschewski, H.; Oechel, A.; Hicke, H. G., Photo-induced graft polymerization surface modifications for the preparation of hydrophilic and low-protein-adsorbing ultrafiltration membranes. Journal of Membrane Science 1996, 115 (1), 31-47.

[23] Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B., Mussel-Inspired Surface Chemistry for Multifunctional Coatings. Science 2007, 318 (5849), 426-430.

[24] Ju, H.; McCloskey, B. D.; Sagle, A. C.; Wu, Y. H.; Kusuma, V. A.; Freeman, B. D., Crosslinked poly(ethylene oxide) fouling resistant coating materials for oil/water separation. Journal of Membrane Science 2008, 307 (2), 260-267.

[25] Steels, B. M.; Koska, J.; Haynes, C. A., Analysis of brush-particle interactions using self-consistent-field theory. Journal of Chromatography B: Biomedical Sciences and Applications 2000, 743 (1), 41-56.

[26] Jo, S.; Park, K., Surface modification using silanated poly(ethylene glycol)s. Biomaterials 2000, 21 (6), 605-616.

[27] McCloskey, B. D.; Park, H. B.; Ju, H.; Rowe, B. W.; Miller, D. J.; Freeman, B. D., A bioinspired fouling-resistant surface modification for water purification membranes. Journal of Membrane Science 2012, 413-414, 82-90.

[28] Ulbricht, M., Advanced functional polymer membranes. Polymer 2006, 47 (7), 2217-2262.

[29] Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Mariñas, B. J.; Mayes, A. M., Science and technology for water purification in the coming decades. Nature 2008, 452 (7185), 301-310.

[30] Li, D.; Wang, H., Recent developments in reverse osmosis desalination membranes. Journal of Materials Chemistry 2010, 20 (22), 4551-4566.

[31] Zhao, J.; Zhao, X.; Jiang, Z.; Li, Z.; Fan, X.; Zhu, J.; Wu, H.; Su, Y.; Yang, D.; Pan, F.; Shi, J., Biomimetic and bioinspired membranes: Preparation and application. Progress in Polymer Science 2014, 39 (9), 1668-1720.

[32] Tang, C. Y.; Zhao, Y.; Wang, R.; Hélix-Nielsen, C.; Fane, A. G., Desalination by biomimetic aquaporin membranes: Review of status and prospects. Desalination 2013, 308, 34-40.

[33] Ji, Y.-L.; An, Q.-F.; Guo, Y.-S.; Hung, W.-S.; Lee, K.-R.; Gao, C.-J., Bio-inspired fabrication of high perm-selectivity and anti-fouling membranes based on zwitterionic polyelectrolyte nanoparticles. Journal of Materials Chemistry A 2016, 4 (11), 4224-4231.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

[34] Shao, Q.; White, A. D.; Jiang, S., Difference of Carboxybetaine and Oligo(ethylene glycol) Moieties in Altering Hydrophobic Interactions: A Molecular Simulation Study. The Journal of Physical Chemistry B 2014, 118 (1), 189-194.

[35] Yong, J.; Chen, F.; Yang, Q.; Huo, J.; Hou, X., Superoleophobic surfaces. Chemical Society Reviews 2017, 46 (14), 4168-4217.

[36] Kuang, Y.; Chen, C.; Chen, G.; Pei, Y.; Pastel, G.; Jia, C.; Song, J.; Mi, R.; Yang, B.; Das, S.; Hu, L., Bioinspired Solar-Heated Carbon Absorbent for Efficient Cleanup of Highly Viscous Crude Oil. Advanced Functional Materials 2019, 29 (16), 1900162.

[37] McNutt, M. K.; Camilli, R.; Crone, T. J.; Guthrie, G. D.; Hsieh, P. A.; Ryerson, T. B.; Savas, O.; Shaffer, F., Review of flow rate estimates of the Deepwater Horizon oil spill. Proceedings of the National Academy of Sciences 2012, 109 (50), 20260-20267.

[38] Meng, X.; Wang, M.; Heng, L.; Jiang, L., Underwater Mechanically Robust Oil-Repellent Materials: Combining Conflicting Properties Using a Heterostructure. Advanced Materials 2018, 30 (11), 1706634.

[39] Guo, T.; Heng, L.; Wang, M.; Wang, J.; Jiang, L., Robust Underwater Oil-Repellent Material Inspired by Columnar Nacre. Advanced Materials 2016, 28 (38), 8505-8510.

[40] Zhang, F.; Zhang, W. B.; Shi, Z.; Wang, D.; Jin, J.; Jiang, L., Nanowire-Haired Inorganic Membranes with Superhydrophilicity and Underwater Ultralow Adhesive Superoleophobicity for High-Efficiency Oil/Water Separation. Advanced Materials 2013, 25 (30), 4192-4198.

[41] Cai, Y.; Lin, L.; Xue, Z.; Liu, M.; Wang, S.; Jiang, L., Filefish-Inspired Surface Design for Anisotropic Underwater Oleophobicity. Advanced Functional Materials 2014, 24 (6), 809-816.

[42] Cai, Y.; Lu, Q.; Guo, X.; Wang, S.; Qiao, J.; Jiang, L., Salt-Tolerant Superoleophobicity on Alginate Gel Surfaces Inspired by Seaweed (Saccharina japonica). Advanced Materials 2015, 27 (28), 4162-4168.

[43] Li, H.; Hao, D.; Fan, J.; Song, S.; Guo, X.; Song, W.; Liu, M.; Jiang, L., A robust double-network hydrogel with under sea water superoleophobicity fabricated via one-pot, one-step reaction. Journal of Materials Chemistry B 2016, 4 (27), 4662-4666.

[44] Lin, L.; Liu, M.; Chen, L.; Chen, P.; Ma, J.; Han, D.; Jiang, L., Bio-Inspired Hierarchical Macromolecule–Nanoclay Hydrogels for Robust Underwater Superoleophobicity. Advanced Materials 2010, 22 (43), 4826-4830.

[45] Xu, L.-P.; Peng, J.; Liu, Y.; Wen, Y.; Zhang, X.; Jiang, L.; Wang, S., Nacre-Inspired Design of Mechanical Stable Coating with Underwater Superoleophobicity. ACS Nano 2013, 7 (6), 5077-5083.

[46] Nonoyama, T.; Wada, S.; Kiyama, R.; Kitamura, N.; Mredha, M. T. I.; Zhang, X.; Kurokawa, T.; Nakajima, T.; Takagi, Y.; Yasuda, K.; Gong, J. P., Double-Network Hydrogels Strongly Bondable to Bones by Spontaneous Osteogenesis Penetration. Advanced Materials 2016, 28 (31), 6740-6745.

[47] Yao, H.-B.; Ge, J.; Mao, L.-B.; Yan, Y.-X.; Yu, S.-H., 25th Anniversary Article: Artificial Carbonate Nanocrystals and Layered Structural Nanocomposites Inspired by Nacre: Synthesis, Fabrication and Applications. Advanced Materials 2014, 26 (1), 163-188.

[48] Addadi, L.; Joester, D.; Nudelman, F.; Weiner, S., Mollusk Shell Formation: A Source of New Concepts for Understanding Biomineralization Processes. Chemistry – A European Journal 2006, 12 (4), 980-987.

[49] Kesel, A.; Liedert, R., Learning from nature: Non-toxic biofouling control by shark skin effect. Comparative Biochemistry and Physiology a-Molecular & Integrative Physiology 2007, 146 (4), S130-S130.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202010_6(10).0048

[50] Bixler, G. D.; Bhushan, B., Rice- and butterfly-wing effect inspired self-cleaning and low drag micro/nanopatterned surfaces in water, oil, and air flow. Nanoscale 2014, 6 (1), 76-96.

[51] Liu, K.; Jiang, L., Bio-Inspired Self-Cleaning Surfaces. Annual Review of Materials Research 2012, 42 (1), 231-263.

[52] Bhushan, B., Bioinspired Structured Surfaces. Langmuir 2012, 28 (3), 1698-1714.

[53] Chien, H.-W.; Chen, X.-Y.; Tsai, W.-P.; Lee, M., Inhibition of biofilm formation by rough shark skin-patterned surfaces. Colloids and Surfaces B: Biointerfaces 2020, 186, 110738.

[54] Carman, M. L.; Estes, T. G.; Feinberg, A. W.; Schumacher, J. F.; Wilkerson, W.; Wilson, L. H.; Callow, M. E.; Callow, J. A.; Brennan, A. B., Engineered antifouling microtopographies--correlating wettability with cell attachment. Biofouling 2006, 22 (1-2), 11-21.

[55] Dundar Arisoy, F.; Kolewe, K. W.; Homyak, B.; Kurtz, I. S.; Schiffman, J. D.; Watkins, J. J., Bioinspired Photocatalytic Shark-Skin Surfaces with Antibacterial and Antifouling Activity via Nanoimprint Lithography. ACS Applied Materials & Interfaces 2018, 10 (23), 20055-20063.

[56] Gao, F.; Baraka-Kamali, E.; Shirtcliffe, N.; Terrell-Nield, C., A preliminary study of the surface properties of earthworms and their relations to non-stain behaviour. Journal of Bionic Engineering 2010, 7 (1), 13-18.

[57] Cui, J.; Daniel, D.; Grinthal, A.; Lin, K.; Aizenberg, J., Dynamic polymer systems with self-regulated secretion for the control of surface properties and material healing. Nature Materials 2015, 14 (8), 790-795.

[58] Zhou, X.; Ma, G.; Zhao, H.; Cui, J., Self-Forming Interlocking Interfaces on the Immiscible Polymer Bilayers via Gelation-Mediated Phase Separation. Macromol Rapid Commun 2017, 38 (17).

[59] Mohan Srinivasarao; David Collings; Alan Philips; Patel, S., Three-Dimensionally Ordered Array of Air Bubbles in a Polymer Film. Science 2001, Vol. 292, Issue 5514, pp. 79-83.

[60] Zhao, H.; Sun, Q.; Deng, X.; Cui, J., Earthworm-Inspired Rough Polymer Coatings with Self-Replenishing Lubrication for Adaptive Friction-Reduction and Antifouling Surfaces. Advanced Materials 2018, 30 (29).

[61] Zhao, H.; Sun, Q.; Deng, X.; Cui, J., Earthworm-Inspired Rough Polymer Coatings with Self-Replenishing Lubrication for Adaptive Friction-Reduction and Antifouling Surfaces. Advanced Materials 2018, 30 (29), 1802141.