REVIEW

# Thermal Spray Coatings for Protection Against Microbiologically Induced Corrosion: Recent Advances and Future Perspectives

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**Abstract** Corrosion has been persisting as the most severe concern for steel structures in the marine environment. Due to the widespread occurrence of biofouling, apart from the electrochemical corrosion, microbiologically induced corrosion (MIC) is an important factor that triggers the deterioration of marine steel infrastructures. Traditional anti-corrosion coatings usually lack the antifouling function, attachment and colonization of marine microorganisms therefore in most cases accelerate the existing corrosion damage. Anti-corrosive coating fabricated by thermal spray has been extensively applied for the marine corrosion prevention, yet the anti-MIC coatings deposited by thermal spray technical route still keep elusive. Developing thermal-sprayed coatings with dual anti-corrosion and antifouling performances is the key to combating MIC. In this review, most recent advances in understanding biofouling and developing antifouling and anti-MIC techniques are surveyed. The formation and evolution of MIC and biofouling, and the effect of microbial biofilm on their occurrence are addressed briefly. Strategies involving the use of chemical methods, physical methods and biological methods to prevent MIC and biofouling are discussed. Selection and design of thermal spray coating materials with desired corrosion resistance and antifouling performances are reviewed. Current perspectives and future possibilities of thermal-sprayed marine coatings for long-term anti-MIC applications are also discussed.

**Keywords** anti-corrosion coatings · antifouling coatings · antifouling mechanisms · corrosion behavior · microbiologically induced corrosion · thermal-sprayed marine coatings

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**Abbreviations**

| | |
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| MIC | Microbiologically induced corrosion |
| GDP | Gross domestic products |
| TBT | Tributyltin |
| IMO | International Maritime Organization |
| EPS | Extracellular polymeric substances |
| QS | Quorum sensing |
| SRB | Sulfate-reducing bacterium |
| SOB | Sulfur-oxidizing bacterium |
| IRB | Iron-reducing bacterium |
| IOB | Iron-oxidizing bacterium |
| EET | Extracellular electron transfer |
| DET | Direct electron transfer |
| MET | Mediated electron transfer |
| FAD | Flavin adenine dinucleotide |
| MICI | Microbiologically influenced corrosion inhibition |
| CDP | Controlled depletion polymer |
| SPC | Self-polishing copolymer |
| HDPE | High-density polyethylene |

SLIPS     Slippery lubricant-infused porous surface
PEG       Polyethylene glycol
PEO       Polyethylene oxide
PDMS      Polydimethylsiloxane
PFA       Perfluoroalkoxy
NPAs      Natural product antifoulants
QQ        Quorum quenching
QSI       Quorum sensing inhibitors
PUF       Poly(urea-formaldehyde)


## Introduction

There have been vast demands for ocean technologies in response to the booming ocean development and ocean resources exploration for economic benefits, for instance the expected global ocean economic benefit is US$3 trillion by 2030 (Ref [1]). For the marine infrastructures, corrosion and biofouling are the two major persisting challenges that have caused huge economic losses. The National Association of Corrosion Engineers predicted that global corrosion costs accounted for 3.4% of global gross domestic products (GDP) in 2016 (Ref [2]). The Chinese Academy of Engineering also announced the economic losses caused by corrosion in China was about US$310 billion in 2014 that accounted for 3.34% of the gross domestic product (Ref [3]). The marine environment contains a lot of microorganisms, which can adhere to the surface of materials to form biofilm and therefore cause biofouling and associated microbiologically induced corrosion (MIC). In most cases, MIC accelerates the degradation of metal alloys and leads to materials failure (Ref [4], [5]). The corrosion caused by microorganisms or related to MIC accounts for 20% of the total corrosion loss of metals and building materials (Ref [6]). MIC usually involves attachment of microorganisms like barnacles and mussels on the material surface with consequent biofilm formation. Apart from the impact on MIC, Schultz (Ref [7]) found that the attachment of large biofouling organisms on ships may increase their navigation resistance by 86%, even the light "slime" pollution secreted by microorganisms such as diatoms would also increase the resistance by 10-16%. Besides, large biofouling organisms attached to the bottom of the ship may cause danger to the surrounding marine organism and result in biological invasion (Ref [8]). Developing efficient antifouling techniques is therefore crucial to inhibit or prevent the attachment and following colonization of microorganisms on marine materials for solving the problems of MIC and biofouling. However, a previous study already showed that the impact of microbial biofilm on the corrosion behaviors of marine steel structures was attributed to synergistic influence by both the biofilm and physicochemical characteristics of the substratum materials (Ref [9]), which

makes the efforts to develop the anti-MIC coatings complicated.

Among the anti-corrosion techniques explored so far, surface coatings made by a variety of processes such as hot dip silicon-plating (HDS), chemical vapor deposition (CVD), physical vapor deposition (PVD) and electrodeposition have been proven effective mainly through physically restricting penetration of corrosive media (Ref [10-14]), while the traditional corrosion-resistant coatings do not take into account the influence of adhered microorganisms on the material surface which in most cases accelerates the corrosion. Combination of the functions of preventing microorganism adhesion and resisting corrosion is considered to be an efficient strategy to prevent MIC. Developing the coatings with the synergistic functions however involves deep understanding of the occurrence of biofouling and corrosion.

To resist the adhesion of marine microorganisms, traditional organic antifouling coatings used toxic biocide such as tributyltin (TBT) as the antifouling agent (Ref [15]). However, the high and non-targeted biological toxicity is also harmful to other beneficial microorganisms and even destroys the normal balance of marine ecosystem (Ref [16], [17]). The International Maritime Organization (IMO) stipulated in 2001 that ships should be completely banned from using TBT as the antifoulant since 2008 (Ref [18], [19]). There has been an urgent need for environment-friendly antifouling coatings. In particular, for anti-MIC coatings, participation of antifoulant is required in most cases, for antifouling activity enhances anti-MIC performances of the coatings apart from their anti-corrosion properties. For fabricating the coatings with multidisciplinary functions, thermal spray processing approach offers the ease of on-site operation, large-scale coating deposition and cost efficiency and has been extensively used for depositing anti-corrosion coatings (Ref [20-22]). In recent years, research efforts have been made by many thermal spray laboratories pertaining to constructing anti-MIC coatings. It has been clear that for development of efficient anti-MIC coatings, appropriate selection of antifouling components for the coatings is essential.

This article reviews the formation mechanisms of marine biofilm and its impact on biofouling and MIC of marine structures. The latest strategies in particular thermal spray deposition of marine coatings to prevent the attachment of microorganisms on material surface are surveyed. Several typical anti-MIC coating strategies were reviewed, including the coatings that delay the release of copper ions to achieve low toxicity and long-term performances, non-toxic textured and superhydrophobic coatings that reduce the adhesion of microorganisms and environmentally friendly coatings containing natural antifoulants. The challenges and opportunities of thermal-sprayed coatings

for anti-MIC applications are discussed. This review is expected to shed light on design and thermal spray fabrication of anti-MIC coatings for protecting marine steel structures for long-term applications.

## The Role of Biofilm in MIC and Biofouling

### Formation Process of Biofilm

When steel marine structures are submerged in seawater, they are usually quickly colonized by bacteria, diatoms and other marine microorganisms on their surfaces for consequent formation of complex biofilm (Ref 23). The biofilm will generate quorum sensing (QS) signals that lead to the attachment of macrofouling organisms (Ref 24). Formation of the biofilm mainly involves four consecutive processes, namely formation of conditioning layers through attachment of marine macromolecules, attachment of bacteria and diatoms, secretion of extracellular polymeric substances (EPS) and regulation of biofilm formation by QS signal of the microorganisms. After the materials are immersed in seawater for several minutes to hours, macromolecules such as polysaccharides, proteins and other organic matter will quickly attach to their surfaces, forming conditioning layer (Ref 25, 26). This layer can change the physical and chemical properties of the material surface, such as surface roughness, wettability and charge, in turn regulating the attachment of bacteria, diatoms and other microorganisms (Ref 27-29) for subsequently occurred MIC. The influence of conditioning layer on the adhesion of bacteria and diatoms to material surfaces have been extensively studied (Ref 30, 31). Conditioning layers are considered crucial to the adsorption and initiation of biofilm. It is reasonably speculated that adhesion of microorganisms on the surfaces for steels is the first direct reason triggering the possible MIC (Ref 32). Understanding and regulation of the adhesion is therefore important for developing efficient anti-MIC coatings.

The main components of biofilm are bacteria and diatoms, and other single-cell organisms account for less than 1% of the total number of biofilm cells (Ref 33). Most of the microorganisms deteriorates the corrosion, causing accelerated corrosion through altering local microenvironment, in some cases, with the formation of pitting (Ref 9). It was found that the initial stage of the biofilm formation involves the attachment of microorganisms, which is only temporary and reversible and is mainly affected by van der Waals force, Brownian motion, electrostatic interaction and acid-base interaction (Ref 34). Because of the limited thickness of the conditioning layer, the attachment of microorganisms was also affected by other physical properties of the substrate such as surface roughness

(Ref 35). Rough surfaces produce low shear zones, which may significantly reduce the force to remove attached bacteria from the surface. In addition, high roughness increases the surface contact area, providing more space for the attachment of microorganisms.

After the adherence of the microorganisms, their secreted EPS are an important part of biofilm. Many studies reported that divalent ions, especially $Ca^{2+}$ and $Mg^{2+}$, promote the initial attachment of marine microorganisms through physical interactions such as neutralization of the double electric layers (Ref 36), reduction of charge repulsion, compression of the double electric layers (Ref 37) and reduction of electron density (Ref 38). Those results give certain clues that antifouling and anti-MIC coatings might attain the anticipated performances through releasing from the coatings of the divalent ions that restrain the attachment of microorganisms in seawater. Recent studies also reported that $Ca^{2+}$, $Mg^{2+}$ may also affect the species adhesion by regulating protein expression and polysaccharide synthesis in secreted EPS (Ref 39). This result indicates that divalent ions still affect the adhesion of microorganisms in the irreversible stage. The accumulation of EPS on the material surface provides a binding site for the adsorption and transport of nutrients and metal ions, which increases the adaptability of biofilm to extreme conditions and deal with the dramatic change of the external environment (Ref 40). Compared with plankton, biofilm is more resistant to antibiotics, disinfectants and metal ions (Ref 41, 42). Dash et al. (Ref 43) discussed the interaction behavior between bacterial EPS and mercury, which is a representative of toxic metals, and found that the protein component in EPS was an active participant in the binding of mercury to EPS. The combination of EPS and mercury can make metal ions no longer interact with microorganisms, thereby reducing the toxicity of the metal ions to microorganisms. The main functional groups in the interaction of EPS with mercury include carboxyl, phosphate, hydroxyl, amino and thiol. Although the adsorption of metal ions by biofilm can solve the problem of serious metal pollution (Ref 43, 44), the existence of biofilm would cause the occurrence of MIC and biofouling. To avoid MIC, it is therefore essential to prohibit the formation of biofilm on the surfaces of steel structures.

### Occurrence Mechanism of MIC and Effect of Biofilm on MIC

Metals are often used as marine structural materials, including pipelines, ships and port facilities. In the marine environment, attachment and further colonization of bacteria, algae and other microorganisms usually result in MIC. Sulfate is a widely distributed electron acceptor in the marine environment. A huge variety of bacteria, mainly

including sulfate-reducing bacterium (SRB), sulfur-oxidizing bacterium (SOB), iron-reducing bacterium (IRB), iron-oxidizing bacterium (IOB), are involved in the water-sulfur cycle and iron cycle. SRB, a kind of anaerobic bacterium, can transmit electrons obtained in the process of oxidizing organic matter to sulfate, and then obtain energy from this process to maintain its growth. SRB is considered as the culprit of MIC due to its high electron transfer efficiency. The loss caused by MIC of steel that is induced by SRB accounts for more than 50% of the total MIC loss (Ref 45). To date, the available mechanisms elucidating the SRB-induced MIC mainly pertain to cathodic depolarization, oxygen concentration cell and extracellular electron transfer (EET) (Fig. 1).

Cathodic depolarization (Fig. 1a) relates to the removal of hydrogen from the cathode area of iron surface and the reduction of $SO_4^{2-}$ by bacterial hydrolase (Ref 46). SRB uses the adsorbed hydrogen in the reduction process of $SO_4^{2-}$ to catalyze the recombination of hydrogen atoms into hydrogen ($H_2$), which improves the cathode reaction rate. Thus, the cathodic reaction depolarization would indirectly accelerate the corrosion reaction. The metabolites of SRB can also affect corrosion, FeS is a common metabolite, and the uneven deposited FeS on steel surface increased the contact area of steel surface and seawater so that more SRB adheres to the steel surface, thereby accelerating pitting corrosion (Ref 47). The oxygen concentration cell model is another typical MIC mode (Fig. 1b). Once the biofilm is formed, respiration of microorganisms in the biofilm consumes oxygen and the dense biofilm hinders the diffusion of oxygen, resulting in low oxygen concentration (anode) in the region. However, the cathode region has high oxygen concentration and it is not covered by the biofilm. Therefore, the oxygen concentration cell forms. At the same
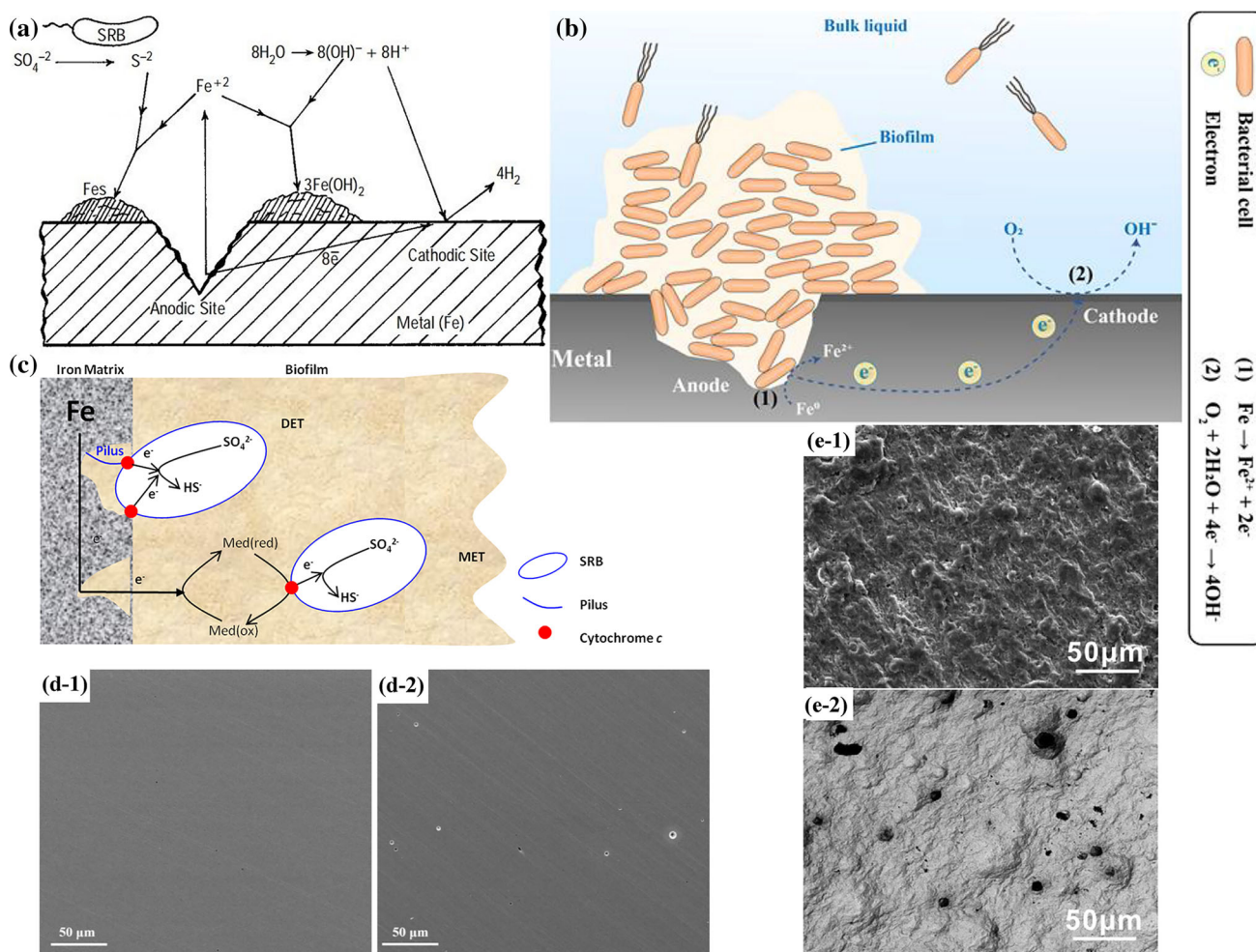


**Fig. 1** Schematic depiction showing the three mechanisms of the MIC and SRB-induced corrosion microstructure of the steel, (a) cathodic depolarization (Ref 46), (b) oxygen concentration cell (Ref 48), (c) extracellular electron transfer (EET) (Ref 52), SEM images of 2205 duplex stainless steel specimens immersed in sterile (d-1) and SRB inoculation (d-2) media for 28 days after removal of biofilm and corrosion products (Ref 55), and SEM images of X65 steel specimens after being immersed in sterile (e-1) and mixed SRB+IOB (e-2) media for 21 days after removal of corrosion products (Ref 58)

time, after the oxygen concentration is reduced, the anaerobic conditions for SRB propagation are gradually formed, and the metal corrosion is in turn accelerated (Ref 48).

The above mentioned two mechanisms relate to the phenomena that SRB obtains electrons and energy from organic species. While studies have shown that SRB can still cause serious corrosion to metals when they are hungry (Ref 49). This is because SRB could directly obtain electrons from the metal substrate. Sulfate in the cytoplasm can be used as an electron acceptor and is decomposed under the action of enzymes. Normal organic matter could diffuse into the cells from the environment, yet insoluble metal substrate $Fe^0$ could not diffuse into the cells. Therefore, the electrons outside the cells must be transported to the cytoplasm for the reduction reaction. This process of electron transfer across cell walls is called extracellular electron transfer (EET) (Fig. 1c) (Ref 50-52). EET has two realization ways, namely direct electron transfer (DET) and mediated electron transfer (MET). For DET, when the sessile cells directly attach to iron, c-cytochrome and conductive nanowires are used as carriers to transmit electrons to cells (Ref 53, 54). The MIC mechanism of SRB on 2205 duplex stainless steel was investigated (Ref 55). Results showed that after the steel was placed in the SRB medium for 28 days, many corrosion pits were seen on the surface (Fig. 1d-2 versus d-1). It was claimed that SRB triggered MIC of the stainless steel through an extracellular electron transfer mechanism (Ref 55). MET refers to the soluble electron transfer medium that absorbs electrons from the metal surface and releases them into the c-cytochrome bound to cell wall. As reported, the main electron transfer media are riboflavin and flavin adenine dinucleotide (FAD) (Ref 56, 57). According to the EET mechanism, it can be explained that the starved SRB biofilm has an aggressive corrosive effect on carbon steel because the bacteria use the extracellular electrons released by $Fe^0$ oxidation as electron donors to accelerate the corrosion when the medium lacks organic carbon (Ref 39). Zhang et al. (Ref 57) found that the addition of electron transfer medium in the medium species increased the corrosion rate, which proved that electron transfer is the bottleneck of MIC.

In the marine environment, microorganisms and their metabolites can directly change the microenvironment at the surfaces of submerged steels. The original seawater/metal interface can be transformed into biofilm/metal interface, so the most destructive corrosion occurs in the presence of multispecies biofilm. For this biofilm, synergistic effects exist due to the different species, which results in more serious corrosion than the biofilm comprising only a single species. For example, Lv et al. (Ref 58) found that after X65 steel was immersed in the medium containing SRB and IOB for 21 days, a large number of corrosion pits were formed on the surface (Fig. 1e-2 versus e-1). It was further realized that consumption of oxygen by the aerobic IOB promotes the growth of anaerobic SRB, in turn accelerating the corrosion (Ref 58). Besides, SRB and SOB can also synergistically accelerate the corrosion of steel (Ref 59). In addition, the thickness of the biofilm with three-dimensional structure is in microns, it can be regarded as a transport barrier and make the pH, dissolved oxygen, ion concentration and organic content in the biofilm different from those in seawater, which in turn accelerates the occurrence of local corrosion. EPS also has an important impact on MIC. EPS comprising huge amount of biological molecules is electronegative and can selectively combine with cations on the steel surface, then form a new redox reaction channel which accelerates the ionization of steel and leads to the dissolution of metal (Ref 60).

However, it should be noted that biofilm has dual effects on occurrence of MIC. Regardless of the fact that biofilm accelerates corrosion of metals in most cases, biofilm can also inhibit the occurrence of MIC through its physical barrier effect in some cases. This barrier phenomenon was first discovered by Iverson (Ref 61). Yet this protection effect is usually realized at early growth stage of biofilm formation, for example early stage biofilm formed by *Bacillus sp.* and *E. coli* bacteria showed enhancing effect on the electrochemical corrosion of arc-sprayed Al coatings in seawater (Ref 62, 63). Most bacteria can inhibit the corrosion of materials when they survive, however the corrosion rate increased after the bacteria died. This phenomenon has aroused the interest of researchers. Dong et al. (Ref 64) found that excessive EPS stimulated the anodic dissolution of carbon steel because $Fe^{2+}$ was combined with polysaccharides in EPS through metal dissolution, but the low concentration of EPS can inhibit the corrosion of carbon steel. The phenomenon that biofilms inhibit microbial corrosion was called microbiologically influenced corrosion inhibition (MICI). Zuo (Ref 65) described three possible mechanisms of MICI, namely removal of corrosive substances through microbial activity, inhibition of the growth of corrosive microorganisms and formation of protective layers through biofilm and EPS, which changes the electrochemical behavior of the interface between metal and biofilm. MICI might be a new environment-friendly method to prevent and treat MIC. However, most of the results of MICI studies were obtained under optimized laboratory conditions, which mainly focused on clarifying the MICI mechanism of a single microorganism (Ref 66). Due to the complexity and diversity of marine fouling species and the dependence of metabolic processes of microorganisms on the environmental factors, MIC is still the main consequence of

microorganisms, resisting their attachment and following biofilm formation is therefore the predominant topic for marine corrosion research community.

In addition, apart from the microorganisms that attach on steel surface for biofilm formation, large fouling organisms are also attracted by the biofilm to settle on the material surface, accelerating the aging of equipment (Ref 67) (Fig. 2). Most MIC is caused by bacteria, but more of the biofouling is the result of interaction between bacteria and algae. Bacteria benefit from oxygen and carbonaceous metabolites produced by algae, and algae benefit from compounds such as vitamin B12 (cobalamin) produced by bacteria (Ref 68, 69). Similar to the effect of biofilm on MIC, some studies have shown that the biofilm promotes or inhibits the settlement of larvae of various invertebrates, which may be related to the physicochemical properties of the matrix. Gawne et al. (Ref 70) explored the effect of biofilm formed on different substrates on the settlement of diatoms and found that the biofilm formed by *Pseudomonas atlantica* reduced the settlement of diatom *Achnanthes longipes* on polystyrene and enhanced their settlement on glass, but had no effect on silicone coating. In addition, other researchers believed that the presence of biofilm changed the physicochemical properties of substrate surface. Zardus et al. (Ref 71) studied the effect of biofilm on the adhesion of invertebrates and revealed that except bryozoan, the adhesion of the other three larvae on biofilm surface got increased significantly. Moreover, Hadfield et al. (Ref 72) compared the settlement behavior of larvae on clean surface with that on biofilm-covered surface and found that the larvae settled on the biofilm surface were more difficult to be removed by turbulent shear force than the larvae precipitated on the clean surface. Further morphological examination showed the blending of bacteria EPS with larvae (Ref 72), evidencing that the biofilm increased the adhesive strength of larvae. The promoted attachment/colonization of large fouling species ultimately brings about worsened MIC.

Previous studies mostly elucidated the effect of biofilm on the attachment of microorganisms from the perspectives of physics and chemistry, and the attachment is the direct cause for occurrence of MIC. The effect of biofilm activity on the attachment of microorganisms was investigated by Lau and Qian (Ref 73). Two types of bacteria, *Roseobacter sp.* and α-subclass *Proteobacteria*, formed biofilm and were treated with formaldehyde or streptomycin to reduce or inactivate the biofilm. After chemical treatment, settlement of the larvae polychaete *Hydroides elegans* on the two biofilms was significantly reduced. Remarkable influence of the biofilms on the attachment of microorganisms was claimed from the perspective of biology. Moreover, Qian et al. (Ref 74) reported that changes in bacterial community characteristics in biofilm affect the attractiveness of biofilm to barnacle larvae, which may determine the behavior of settling larvae (attachment or detachment). There are many kinds of microorganisms in the marine environment, and fouling organisms have different responses to biofilm formed by different microorganisms. This phenomenon could be explained by the quorum sensing (QS) mechanism (Ref 75). QS is mainly completed by the release of microorganisms and the detection of QS signals, and most QS signals in the marine environment are N-acyl homoserine lactone (AHL) secreted by Gram-negative bacteria (Ref 76). Signal specificity of AHLs comes from their side chains with different lengths (4-18 carbons), saturation and substituent R groups (Ref 77). AHLs are produced by the LuxI protein (or LuxI-type AHL synthase enzymes) from S-adenosyl methionine and the intracellular pool of acyl-carrier proteins. After the synthesis of AHLs, they would cross the bacterial membrane, and then passively re-enter the bacterium through the diffusion of short chain AHLs or actively re-enter the bacterium through the transport of long chain AHLs (Fig. 3a) (Ref 78). Once the concentration of AHLs reaches a certain threshold level, they bind to cytoplasmic luxR-type receptors, stimulating the formation of active dimers and the activation of QS gene transcription responsible for luminescence, biofilm formation, virulence and other related processes (Fig. 3b). When the concentration of AHLs is low, LuxR protein is rapidly degraded except the structure binding to AHLs, which is relatively stable and difficult to be degraded (Ref 79). LuxR-AHLs are one of the most characteristic QS

**Fig. 2** Schematic diagram showing the growing process of marine biofouling by adherence of large species (Ref 67)
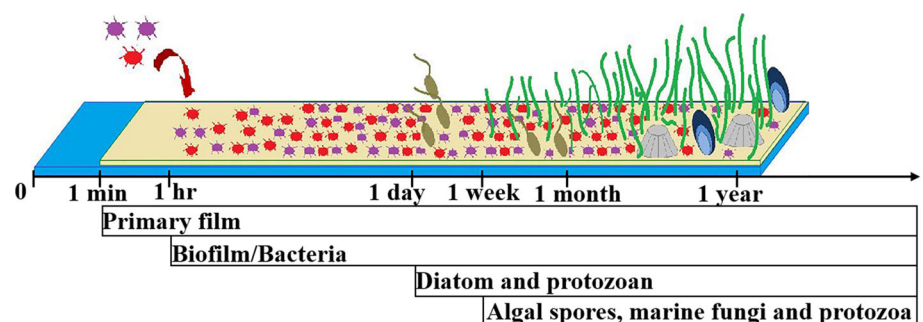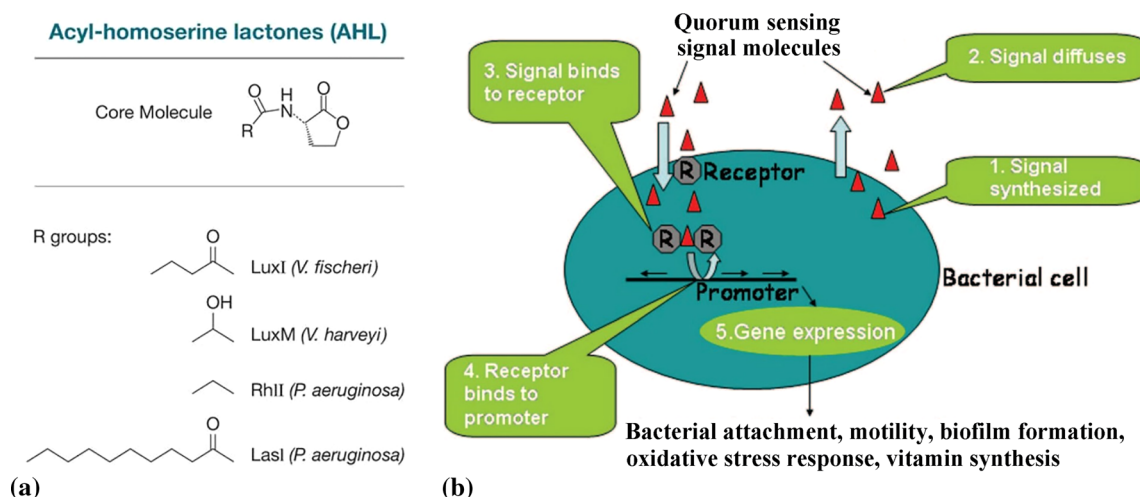
**Fig. 3** Effect of biofilm on the attachment of microorganisms through quorum sensing, (a) AHLs signal molecules (Ref 78) and (b) schematic diagram of AHLs-mediated quorum sensing in Gram-negative marine bacteria (Ref 75)

signal systems and have been identified in more than 70 bacteria (Ref 80. QS signals also play an important role in the interaction between different bio-species. Eukaryotes can detect and respond to bacterial QS signals. Spoerner et al. (Ref 81) found that three bacteria secrete the regulators similar to auxin that allowed cell-to-cell communication between bacteria and algae. Dimitrieva et al. (Ref 82) also reported that catalase produced by the bacterium *Pseudoalteromonas porphyrae* promoted the growth of alga *Laminaria japonica*. QS directly controls biofilm formation and indirectly affects larval attachment through biofilm. There is evidence that the colonization of macrofouling organisms is regulated by the development of bacterial biofilm, such as polychaete *Hydroides elegans* and *Ulva*. The spores of these organisms can detect acyl homoserine lactones as positive clues for colonization (Ref 83, 84).

MIC and biofouling usually occur at the same time, MIC is mainly caused by micro-level corrosion of materials, while biofouling is in macro-level (Ref 85). Both biofouling and MIC are closely related to the formation of biofilm. Therefore, controlling the formation of biofilm is very important to prevent MIC and biofouling. The traditional marine protective coatings only have anti-corrosion performances and lack antifouling functions, while the MIC is caused by the colonization of microorganisms and the formation of biofilm. Adding antifouling function in anti-corrosion coating is an important measure to accomplish the anti-MIC performances. To date, most MIC-prevention strategies have been concentrated on regulating the initial stage of biofilm formation such as preventing microorganisms from attaching or killing microorganisms. Once the biofilm is formed, the biofilm has a protective effect on the microorganisms, which diminishes the effect of the antifouling strategies. Fortunately, although microbial methods, for instance MICI and QS control, are still in the laboratory stage to tackle the biofilm problem, they already showed great potential for practical applications to combat MIC.

Thermal spray, such as plasma spray, high-velocity oxygen-fuel spray, arc spray, flame spray, suspension spray and cold spray, has been successful in depositing both structural and functional coatings for extensive applications (Ref 86). The diversity of the thermal spray methods and raw materials offers great advantages in accomplishing fabrication of various coatings with specific structural designs. Thermal-sprayed environmental-friendly anti-MIC and antifouling coatings have been reported for long-term marine applications.

## Thermal-Sprayed Anti-MIC Coatings

Preventing biofilm formation is of great significance to inhibit MIC. The strategies for antifouling and anti-MIC mainly involve three methods, namely chemical method, physical method and biological method.

### Chemical Method

The chemical method pertains to fabricating biocides-containing polymer coatings with the functions of killing microorganisms. The most extensively used biocide-containing polymer coatings attain their antifouling and anti-MIC functions through the release of biocides (Fig. 4). Polymer-based antifouling and anti-MIC coating can be divided into three categories, i.e., contact leaching coating, controlled depletion polymer coating (CDP) and self-
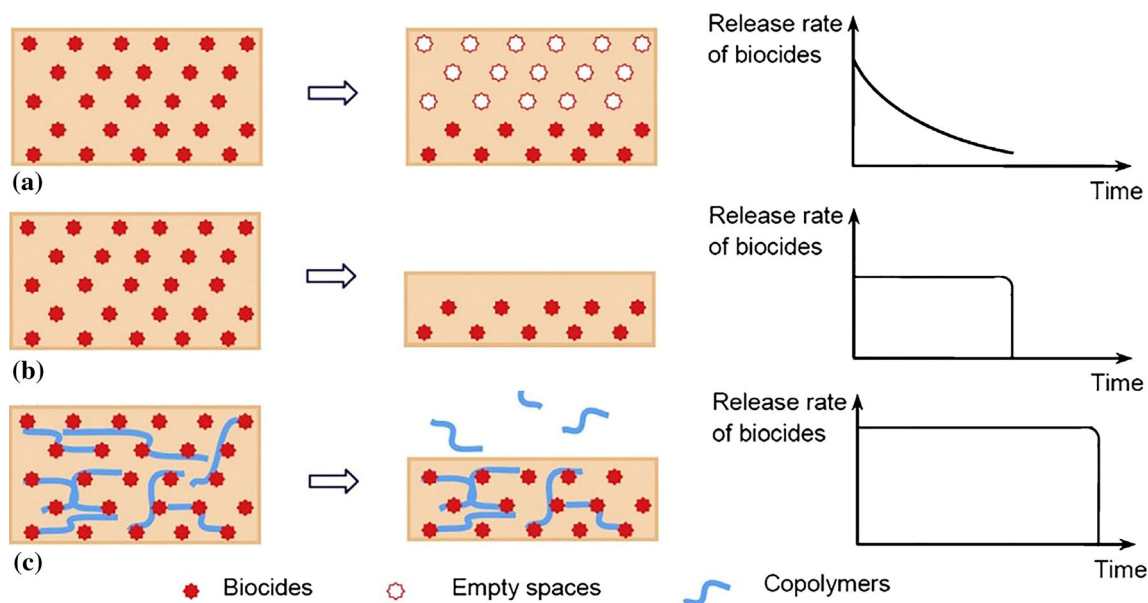
**Fig. 4** Scheme illustration of the behavior of biocide-based antifouling system (Ref 87, 88), (a) contact leaching coating, (b) controlled depletion polymer coating and (c) self-polishing copolymer coating

polishing copolymer coating (SPC) (Ref 87, 88). Contact leaching coating is composed of insoluble matrix (e.g., epoxy resin) and biocides (Fig. 4a), biocides are gradually released from the coating and the holes formed during coating fabrication. Seawater can penetrate into the holes and dissolve deeper biocides. As reported by Fu et al. (Ref 89), the epoxy coating loaded with clay nanotubes that are pre-loaded with biocides was prepared and claimed that the release time of biocides could be extended to 12 months, while the protection period of the biocide-containing epoxy coating was only 2-3 months. However, the 12 months protection against biofouling is far from enough for marine infrastructures. To tackle this problem, controlled depletion polymer coating based on rosin and its derivatives was developed (Fig. 4b). Associating with dissolution of the CDP coating matrix, biocides always appear on the surface of the coating for continuous release into the seawater for excellent antifouling performances. Among the polymer-based coatings, the SPC coating showed the best antifouling properties (Fig. 4c), for the release rate of biocides can be controlled by the polymerization degree of the coating and the hydrophilicity of copolymer binders. The service life of SPC coating can reach 5 years, as a typical SPC coating, the tributyltin self-polishing copolymer coating (TBT-SPC) has been dominating the antifouling coating market for decades (Ref 15). However, tributyltin is toxic and difficult to degrade in the marine environment, which threatens the marine ecological environment. Therefore, the use of TBT antifouling coatings was banned by IMO. A large number of copper-based compounds were then developed to substitute for TBT. Cuprous oxide ($Cu_2O$)

was used as the main biocide in commercial antifouling coatings, regardless of the lower copper toxicity than TBT. However, it is reported that marine microalgae can rapidly absorb copper in seawater, causing harm to marine microalgae (Ref 90). Therefore, it is important to control the concentrations of copper in the marine environment to alleviate its negative impact. This nevertheless raises the requirements for extensive research efforts on designing the incorporation means for the biocide with appropriate dosage into the antifouling coatings with desired composite structures. Rapid release of biocides would result in rapid and premature depletion of antifouling activity of the coatings and unnecessarily high biocide concentrations in the marine environment. However, the release rate should not be too slow, since low concentration of biocides causes ineffectiveness. Thermal spray is competitive in making the copper-containing coatings with desired microstructural features. A variety of copper-containing antifouling coatings can be fabricated by different thermal spray methods using different coating materials.

As reported by Tian et al. (Ref 91), a novel Cu-Ti composite coating with micron-scaled laminating structure was fabricated by plasma spraying mechanically blended Cu-Ti powder, their results showed that Cu-Ti in the coating formed a micro-galvanic cell, and the cell changed copper into copper ions. After the copper ions are dissolved, they are in situ encapsulated into the microchannel to achieve a slow release of copper ions and self-polishing performances (Fig. 5a). To accurately control the release rate of copper ions, Tian et al. (Ref 92) prepared Cu-Ti composite coatings with different copper contents. It was
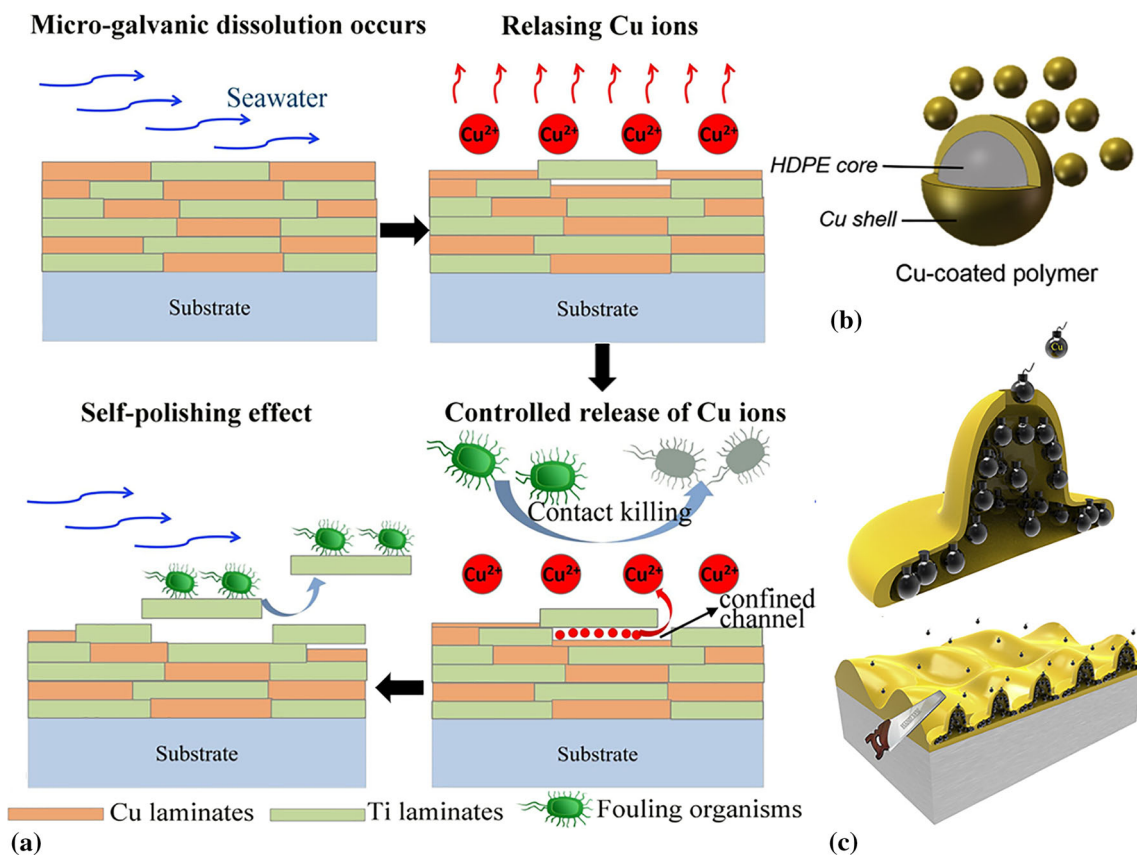
**Fig. 5** Schematic illustration of the thermal-sprayed anti-MIC coatings with controllable release of Cu ions, (a) plasma-sprayed Cu-Ti coating with laminating structure (Ref 91), (b) flame-sprayed Cu-HDPE coating using the Cu-HDPE core-shell powder (Ref 95) and (c) liquid flame-sprayed polyimide-Cu coating with enwrapped structure for controlled release of Cu (Ref 96)

claimed that copper content affected the release rate of copper ions and the self-polishing rate of the Cu-Ti coatings. Therefore, the coatings with different copper contents were prepared to attain appropriate copper ion release rate and self-polishing rate to meet different application requirements.

Compared with plasma spraying, arc spraying is widely used in industry because of its high deposition efficiency and low cost. Fang et al. (Ref 93) reported the deposition of Al-Cu coating by cored wire arc spraying Al-nano-Cu composites. During the coating deposition, Cu nanoparticles reacted with Al, the reaction product Al$_2$Cu slowed down the rapid release of Cu into the environment. It was found that the addition of Cu did not significantly reduce the corrosion resistance of the coatings, while significantly improved the resistance against the colonization of *E. coli* and *Bacillus sp.* To make the coatings with excellent antifouling and anti-corrosion properties, Wang et al. (Ref 94) developed aluminum-polymethyl methacrylate-copper (Al-PMMA-Cu) composite coating as fabricated by cored wire arc spraying. The electrochemical reaction of Cu-Al galvanic cell controlled the release of Cu ions and produced aluminum corrosion products with needle-like

topographical structures, which inhibited the adhesion of *E. coli* to the coating surface. Moreover, PMMA located in the pores of the coatings enhanced their corrosion resistance.

In addition to the metal-based anti-MIC coatings, organic/inorganic composite coatings have also been attempted to slow down the releasing of antifouling Cu ions. According to Jia et al. (Ref 95), Cu/high-density polyethylene (HDPE) particles with core-shell structures as prepared by electroless plating were used as the raw material to prepare antifouling coating by flame spraying (Fig. 5b). The coating showed dense microstructure, which could delay the release of Cu ions. Additionally, Liu et al. (Ref 96) developed polyimide-Cu composite coating by liquid flame spraying and the structure of individual splats was characterized. Polyimide splats had a hollow structure, and Cu nanoparticles were enwrapped in the polyimide shell (Fig. 5c). This study reported that the coating had the ability to control the release of Cu ions and showed a significant ability of resisting the adhesion of *E. coli*, *Bacillus sp.* and algae. Vucko et al. (Ref 97) developed an innovative method to cold spray Cu powder on HDPE and nylon. The in-flight Cu particles with high speed were

embedded into the polymer substrate. The release of Cu ions from the HDPE coating was elongated, since the Cu particles were embedded deep in the soft HDPE. This is inspiring since long-term antifouling activity is essential for anti-MIC performances of the coatings.

## Physical Method

To avoid the occurrence of MIC, another approach involves the measures to prevent the attachment of bacteria/algae and other microorganisms on material surface or reduce the adhesive strength of the microorganisms. Extensive research efforts have been devoted to developing a variety of surface modification techniques. Many functional surface coatings have been proven effective in resisting the attachment of microorganisms, for example superhydrophobic coatings, hydrophobic coatings, hydrophilic coatings, amphiphilic coatings, slippery lubricant-infused porous surface (SLIPS) and micro-patterned surfaces. These coatings do not involve the use of toxic biocides, rendering environmentally friendly characteristics.

Design of superhydrophobic coatings was originally inspired by the lotus effect, and developing low surface energy materials with micro-/nano-sized topographical structures has been the predominating technical route. For antifouling and anti-MIC applications, liquid can easily roll down from the superhydrophobic surface and takes away the microorganisms adhered on the surface to keep the surface clean, and thus inhibits the formation of biofilm (Fig. 6a) (Ref 98). Superhydrophobic coatings usually have anti-corrosion performances because air is usually stored in the micro/nanostructures to form an air layer to reduce the contact area between coatings and seawater. The surface energy and morphology with micro-/nano-sized structures are the decisive variables of the superhydrophobic coatings. Superhydrophobic coatings have been successfully constructed on various metallic substrates (e.g., aluminum, magnesium, stainless steel, etc.) (Ref 99-101). However, the topographical micro/nanostructures of superhydrophobic coatings are highly susceptible to damage by external mechanical force. Some hydrophobic materials for instance fluoropolymers and silicone-based polymers with the contact angles less than 150° are also able to inhibit microbial adhesion. According to Baier (Ref 102), within a certain range of surface energy (20-30 mJ/m$^2$), the adhesion of microorganisms is controllable. Additionally, elastic modulus is another key factor that influences microorganism adhesion on the surface. It was found that the adhesion of microorganisms was proportional to the square root multiplied by elastic modulus (E) and surface free energy ($\gamma$) (Ref 103). Some hydrophobic materials like fluoropolymers and silicone-based polymers have low elastic modulus and surface free energy, thus the attached species can be easily detached from the hydrophobic surface, but the low surface energy limits the bonding strength between the coating and the substrate, usually making easy peeling-off of the coating during the rapid motion. The bonding strength between coating and substrate could be improved by adding an interlayer by establishing chemical reaction at the coating-substrate interface. These interlayers usually contain groups, e.g., alkoxy, epoxy, amino residues, etc., that are easy to react with silicone and epoxy substrate
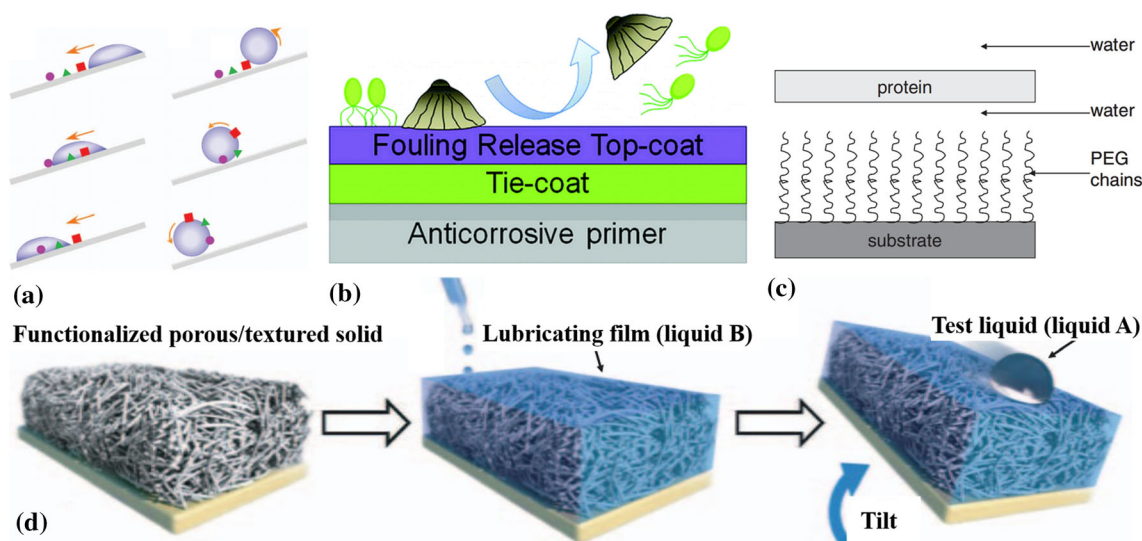


**Fig. 6** Depiction of the functionalized surfaces for preventing the attachment of microorganisms, (a) self-cleaning superhydrophobic coating (Ref 98), (b) fouling release hydrophobic coating to reduce the adhesive strength (Ref 104), (c) hydration layer formed on the surface of hydrophilic coating inhibits the attachment of microorganisms (Ref 112, 113) and (d) self-cleaning, self-healing slippery lubricant-infused porous surface (SLIPS) (Ref 121)

(Fig. 6b) (Ref 104). Esfandeh et al. (Ref 105) reported the use of different silicone alkyl materials as interlayer between silicone coating and epoxy aluminum coating for improving the bonding strength. For the samples without interlayer, the bonding strength was only 431 kPa, while the bonding strength was increased to 2097 kPa after using the interlayer. Even though the hydrophobic coatings have broad prospects for inhibiting microorganism attachment in dynamic marine environments, their poor antifouling activity persists as a major concern. In addition, the hydrophobic coatings are relatively soft and can be easily damaged (Ref 106).

Many studies have shown that the surfaces of hydrophilic polymers such as polyethylene glycol (PEG) and polyethylene oxide (PEO) have a hydration layer that resists the adsorption of proteins and the adhesion of microorganisms (Ref 107-111). To accomplish attachment, microorganisms must break through the hydration layer to reach the substrate. The hydration layer increases the difficulty of the adhesion of fouling organisms on the coating surface (Fig. 6c) (Ref 112, 113). However, it should be noted that various microorganisms have different preferences for hydrophilic and hydrophobic surfaces, *Ulva sporelings* weakly adhere to hydrophobic coatings while *Navicula* adhere strongly to hydrophobic coatings (Ref 114, 115). Due to the diversity of marine microorganisms and the complexity of the marine environment, the amphiphilic surfaces with hybrid hydrophobic/hydrophilic properties have been investigated. Promising prospect of the surfaces in fouling release applications has been reported (Ref 116, 117). Amphiphilic materials can incorporate hydrophilic segment (e.g., polyethylene glycol, PEG) to resist the microorganism adhesion and hydrophobic segment (e.g., polydimethylsiloxane, PDMS) to reduce adhesion strength (Ref 118). In addition, the hydrophilic/hydrophobic segment of amphiphilic polymers has poor compatibility and the microphase separation occurs in the two segments transition region, making their surface a complex topological structure to effectively prevent the adhesion of biological macromolecules such as proteins (Ref 119). As reported by Martinelli et al. (Ref 120), polystyrene brushes with amphiphilic side chains (polyoxyethylene-polytetrafluoroethylene) were synthesized. The coating was divided into spherical phase separation zone and horizontal columnar phase separation zone, being attributed to the different hydrophilic/hydrophobic components. After being immersed in water, the surface became rough and the nanoscale inhomogeneity increased. It was realized that the amphiphilic coatings resisted the settlement of *Ulva sporelings* and *Navicula* and reduced their adhesive strength.

Inspired by the structure of *Nepenthes*, Aizenberg et al. (Ref 121) from Harvard University first proposed the concept of slippery lubricant-infused porous surface (SLIPS) in 2011. SLIPS is a liquid surface obtained by injecting perfluorinated lubricants on rough and porous substrates. Three principles for preparing SLIPS were proposed (Ref 121), (1) the lubricant must be wetted and adhered to the substrate stably, (2) solids must be preferentially wetted by lubricants rather than excluded liquids, and (3) the lubricant must not be mixed with the rejected liquid. The most common way to prepare SLIPS is therefore to inject low surface energy lubricants into porous superhydrophobic surfaces (Fig. 6d). Droplets can be quickly removed from the SLIPS because the surface is filled with lubricant with smaller rolling angles. Moreover, liquidity of lubricants can provide self-healing property for SLIPS. It is not surprising that SLIPS showed great potential in preventing the attachment of bacteria and green microalgae in seawater (Ref 122, 123). Wang et al. (Ref 124) fabricated SLIPS coatings using three types of lubricants for anti-MIC inhibition on aluminum, and SRB settlement was inhibited in static and dynamic environments, and the reason for anti-MIC is liquid-like property rather than types of lubricant. In other words, the type of lubricant has little effect on the antifouling function of the coating, what is important is that the lubricant is a flowing liquid. Some lubricants were injected into the porous coatings to obtain antifouling properties without affecting the transparency of the coatings. Wang et al. (Ref 125) developed a novel SLIPS coating on slide glass by pouring lubricant perfluoropolyether over the superhydrophobic surface. The microorganisms attaching to the modified SLIPS surface are easily washed away from the liquid environment and the modification of SLIPS improves underwater transparency of glass samples in the wavelength range of 500-800 nm. The transmittance of SLIPS coatings has great application prospect in the glass components of underwater facilities. The challenge yet is how to make the desired SLIPS structure using the materials with sufficient strength.

The skins of some animals and the leaves of certain plants also have the characteristics of anti-adhesion of microorganisms and self-cleaning, such as shark skin, rice leaves and butterfly wings (Ref 126, 127). Inspired by the natural surfaces, many surface-patterning coatings have been developed to inhibit the adhesion of microorganisms. Polydimethylsiloxane (PDMS) is a commonly used non-toxic elastomer material that has been widely used in the preparation of patterned coatings. Sullivan and Regan (Ref 128) produced *Scyliorhinus canicula* structure coatings by template method on polydimethylsiloxane (PDMS) to prevent microorganism attachment. Additionally, Carman et al. (Ref 129) constructed engineered pillars, ridges and Sharklet AF^TM structures on PDMS elastomer materials. Results showed that the patterns with the width of less than 2 μm or complex Sharklet AF^TM structure can reduce the

attachment percentage of the microorganisms to 15%. The reason for the patterned coating with the capability of inhibiting microorganism attachment lies in the attachment point theory: the more attachment points between microorganisms and coating, the greater adhesion strength. The scale of the topographical microstructure of the patterned coatings is generally smaller than that of the microorganisms, the size is generally unfavorable for microorganism attachment and causes limited attachment point (Ref 130, 131). While the micro-patterns promoting the attachment of microorganisms have also been reported. According to Feng et al. (Ref 132), nanopores with different diameters were prepared on the surface of alumina by anodization. Bacterial adhesion and biofilm formation on the anodized alumina surface with 15 or 25 nm pores were reduced, while bacterial adhesion on the alumina surface with 100 nm pores was even higher than that on nanosmooth surfaces. Specific antifouling mechanisms of the surface-patterning coatings keep unclear.

Thermal spray has been extensively attempted to fabricate the coatings with the abovementioned antifouling/anti-MIC functions. Fabrication of the biocide-free coatings by thermal spraying has been explored. According to Chen et al. (Ref 133), aluminum coatings with micro-patterns were constructed by flame spraying (Fig. 7a). In that study, silicone elastomer was brushed on the surface of the micro-patterned coating, and the amphiphilic ions were modified, which significantly inhibited protein adsorption and diatom attachment. Moreover, the micro-patterns facilitated the antibacterial adherence of the coatings. Additionally, He et al. (Ref 134) reported fabrication of porous needle-like nano-alumina on the surface of arc-sprayed aluminum coating through steam sterilization treatment at 120°C (Fig. 7b). The structural characteristics of micro-/nano-sized alumina had a synergistic effect on inhibiting the attachment of *Chlorella*. It seems clear that for thermal-sprayed anti-MIC coatings, combination of physical and chemical methods is a more effective way than either of them. As reported by Zhai et al. (Ref 135), a hydrophobic perfluoroalkoxy (PFA)/nano-silver (Ag) coating was prepared by suspension flame spraying on aluminum substrate. Synergistic inhibition of bacterial adhesion by hydrophobic interaction of PFA and toxicity of silver nanoparticles was accomplished. These reports further prove the feasibility of thermal spray in constructing the antifouling/MIC coatings using a variety of materials.

## Biological Method

Apart from the physicochemical methods, biological treatment also showed promises for anti-MIC functions. In the marine environment, some bioactive molecules
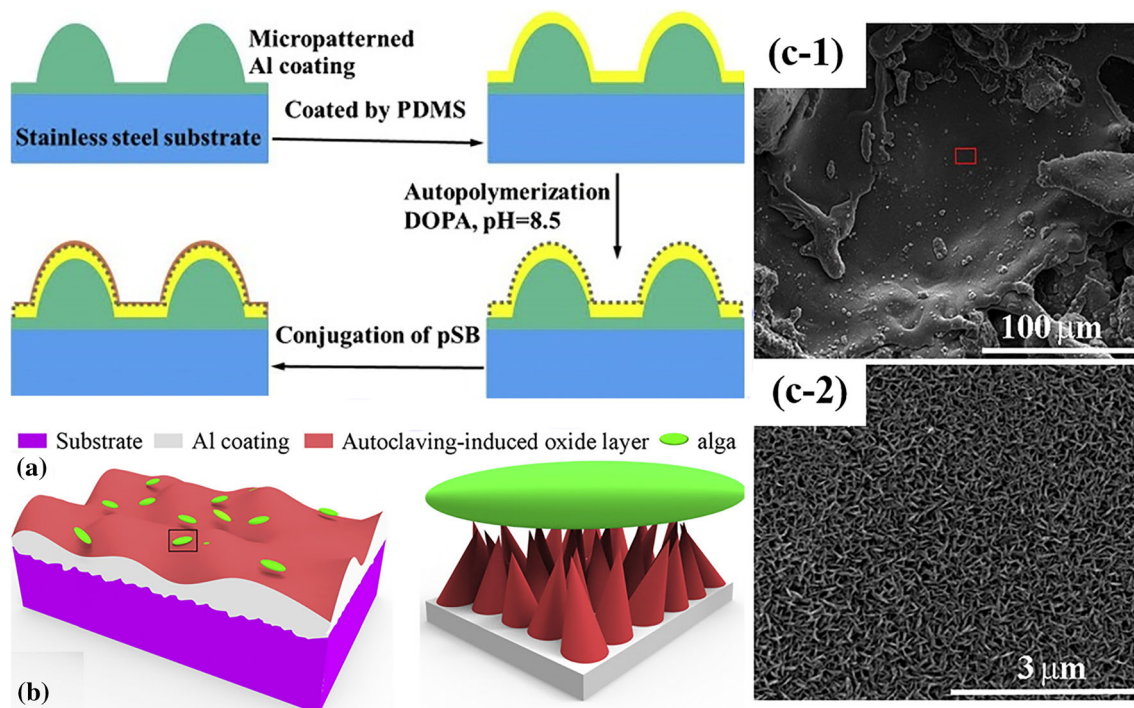


**Fig. 7** Patterned surfaces of thermal-sprayed coatings for preventing microorganism attachment, (a) depiction of the flame-sprayed topological structure with additional chemical modification (Ref 133), (b) depiction of the fabricated porous needle-like nano-alumina on the surface of arc-sprayed aluminum coating by steam sterilization treatment at 120°C (Ref 134) and (c-1, c-2) SEM images of the porous needle-like nano-alumina (c-2 is magnified view of the boxed area shown in c-1)

secreted by certain species can inhibit the attachment of other microorganisms. These secretions such as enzymes and natural product antifoulants (NPAs) can be easily degraded and environment-friendly and have been extracted from various marine organisms (Ref 136). Enzymes and catalytic proteins that are ubiquitous in nature have been found to inhibit microorganism attachment. A study reported by Qian et al. (Ref 137) showed that 0.5 ng/ml protease extracted from *Pseudoalteromonas issackenkonii* can inhibit 50% of the attachment of *Bugula neritina*, exhibiting excellent antifouling properties. In addition, Tasso et al. (Ref 138) found that protease secreted by Bacillus subtilis significantly reduced the attachment of *Balanus amphitrite* Barnacle Cyprids.

The influence of enzyme on biofilm formation was interpreted by direct effect and indirect effect (Ref 139). The direct effect mainly refers to the killing of microorganisms and the degradation of adhesives secreted by microorganisms (Fig. 8a, b). Pettitt et al. (Ref 140) found that serine proteases had an obvious degradation effect on adhesives. Additionally, Aldred et al. (Ref 141) stated that the reason for serine proteases to inhibit the settlement of barnacle is the reduced bacteria adhesion rather than its toxicity. The indirect effect is that enzymes can convert compounds in seawater or substrate/coating to biocides to kill microorganisms (Fig. 8c, d) (Ref 142). The use of biocide-containing coatings will ultimately lead to short service life and environmental problems due to the rapid release of biocides. While enzyme reaction can control the synthesis rate of biocides so as to control their release rate to achieve low toxicity and long-term function. Haloperoxidase has been tried to be added to coatings, since it can convert halide ions and hydrogen peroxide in seawater into effective biocide hypohalogenic acid (Ref 143). Moreover, Hamade et al. prepared antifouling coatings by incorporating tricaprin and lipase into PMMA (Ref 144). The coatings were immersed in seawater with a depth of 1 m for 3 months, and there was no fouling adhesion on the surface.

As discussed previously, QS plays an important role in the formation of biofilm and AHLs are the main QS signal. Thus, interference with the QS process to reduce the attachment of fouling organisms could be a feasible method (Fig. 9). Some enzymes have been found to be able to degrade AHLs to block QS and inhibit microorganism attachment, which is called quorum quenching (QQ). According to the different groups of the degraded AHLs molecule, the enzymes can be divided into three types (Fig. 9b): lactonase, acylase and oxidase/reductase (Ref 78). In some cases, the short-term inhibition effect of some microorganisms has been proven, but long-term efficiency has not been reported, since the enzyme is essentially a protein that is prone to structural changes and loss of activity under extreme conditions such as heat, acid and alkali. Therefore, Olsen et al. (Ref 139) proposed four requirements for enzyme-based coatings, (1) the enzyme must remain active when mixed with coating components, (2) the enzyme should not deteriorate the coating property, (3) the enzyme must have broad-spectrum antifouling effect, and (4) the enzyme activity must have long-term stability in both the dry coating and the wet coating (after immersion in seawater for the marine applications). Another QS blocking method uses small molecule analogs that can compete with signal molecules, which binds to LuxR but not activate them. These small molecules are called quorum sensing inhibitors (QSI). The first QSI compound was isolated from red macro-alga *Delisea pulchra*. These algae can secrete furanones similar to the bacterial AHLs signal, which can inhibit the growth of
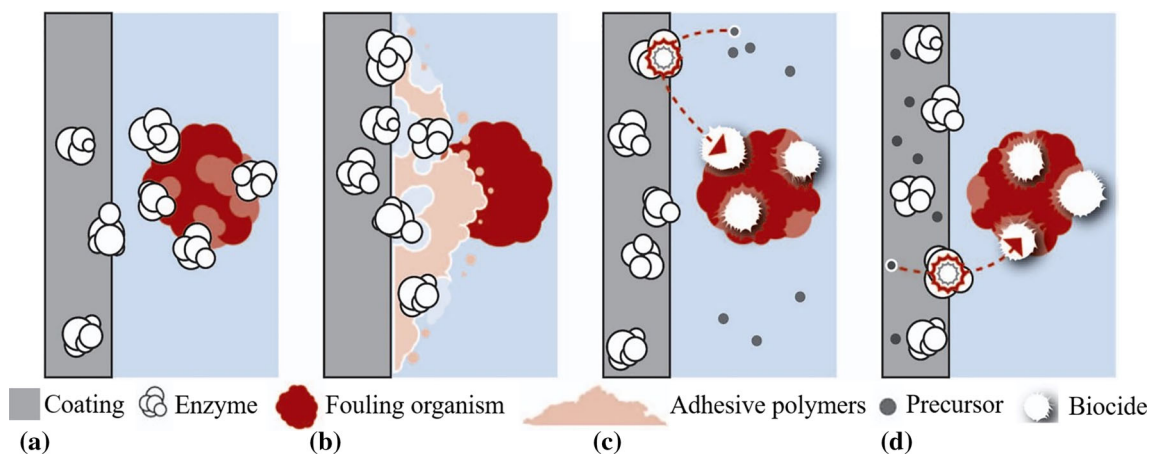


**Fig. 8** Schematic illustration showing the antifouling mechanisms of enzymes, (a) enzymes kill microorganisms, (b) enzymes degrade adhesives of biofilm, (c) enzymes obtain biocides from the environment to kill microorganisms and (d) enzymes obtain biocides from the substrate to kill microorganisms (Ref 139)
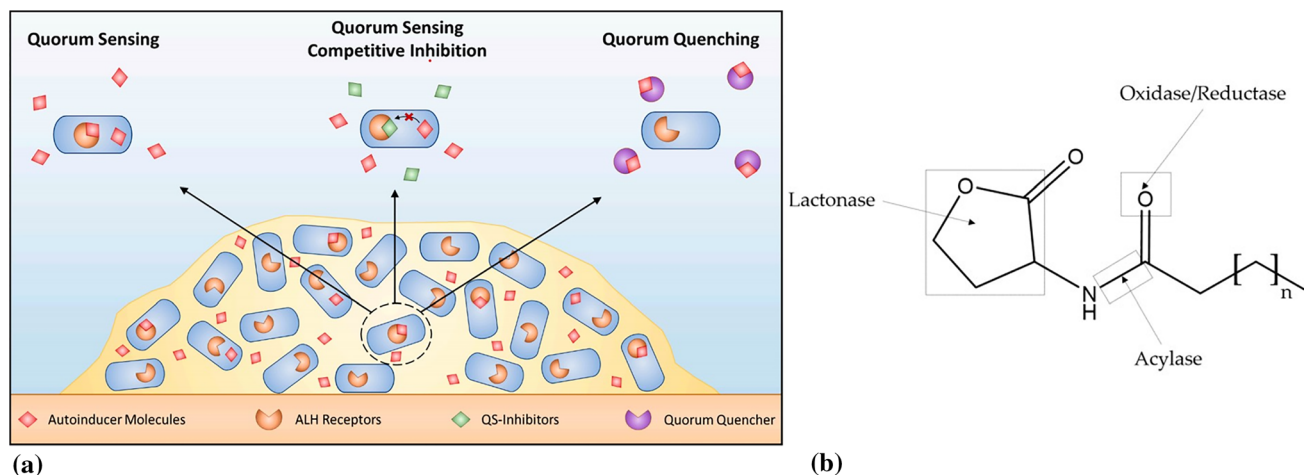
**Fig. 9** (a) AHL-dependent QS in biofilm (left) can be blocked by competitive QS inhibitors (middle) or quorum quenching enzymes (right) (Ref 147), (b) schematic representation of the AHL-degrading enzyme targets. The dotted lines mark position of possible cleavages of N-butyryl-l-homoserine lactone (C4-HSL) molecule by lactonase, acylase and oxidase/reductase (Ref 77)

Gram-negative bacteria and the settlement of invertebrate larvae (Ref 145-147).

In recent years, active antifouling substances extracted from natural products have been found to own the functions of inhibiting microorganism attachment (Ref 148). Capsaicin (8-methyl-vanillyl-6-nonenamide), an extremely spicy vanillin amide alkaloid extracted from pepper, onion and other substances, is considered to be one of the most promising NPAs. Capsaicin has been proven to have antibacterial effect. In addition, capsaicin has a natural irritant odor, which can prevent marine animals from attaching to the marine structure and is harmless to the environment (Ref 149, 150).

Composite coatings containing capsaicin have been developed, and their performance of preventing microorganism attachment is obvious. However, the rapid release of capsaicin shortens the service life of the coatings (Ref 151). The release of capsaicin must therefore be limited through appropriate design of the coating structures. Lu et al. (Ref 152) blended capsaicin with $CoFe_2O_4$/gelatin nanospheres, effectively prolonging the service life of capsaicin. In addition, gelatin nanospheres formed oriented nanostructures on the surface. The coating had obvious inhibitory effect on the settlement of typical fouling organisms because of capsaicin and the oriented nanostructure. A study by Li et al. (Ref 153) reported successful synthesis of capsaicin/silicone oil/poly(urea-formaldehyde) (PUF) microcapsules by mini-emulsion polymerization, and the microcapsules were added to zinc acrylate resin and iron oxide red for coating preparation. The microcapsules alleviated the releasing of capsaicin, resulting in a long-term antifouling effect of the coating. A recent study reported by Liu et al. (Ref 154) showed the encouraging potential of thermal spraying for fabricating the coatings

containing NPAs. High-density polyethylene (HDPE)/capsaicin composite coatings were prepared by flame spraying (Ref 154). The distribution of capsaicin in the coating was uniform, and it had a significant inhibitory effect on the attachment of Gram-negative *E. coli* and Gram-positive *Bacillus sp.* Enzymes like capsaicin could be easily destroyed during high-temperature processing. Liu et al. successfully prepared the capsaicin-containing coatings by flame spray (Ref 154), enlightening the use of thermal spray approach for fabrication of polymer-based anti-MIC coatings containing enzymes and other non-toxic NPAs.

## Conclusions and Future Perspectives

Corrosion and biofouling are the two major obstacles for marine steel infrastructures for long-term functional services. The attachment and following colonization through formation of biofilm of microorganisms usually trigger MIC, which further significantly deteriorates the corrosion of steel structures in the marine environment. Controlling the attachment of microorganisms and avoiding the formation of microbial biofilm is the key to alleviating MIC. Among various surface protection techniques, thermal spray is a simple, cost-efficient and large-scale method for fabrication of protective coatings. Through the appropriate selection of coating materials and the design of desired coating structure, anti-MIC coatings with low toxicity and long-term performances can be achieved. By using various thermal spray methods, metallic composite coatings with the micro-galvanic cell effect, polymer coatings containing biocides for controllable release of the biocides, superhydrophobic coatings and micro/nano-textured coatings have

been successfully fabricated for potential anti-MIC applications. It should be noted that although some progress has been made in suppressing biofouling and MIC, the knowledge of biofouling and MIC is yet insufficient, and understanding of the influence of microbial biofilm on occurrence of MIC is far from final verdict. Extensive research efforts are needed to elucidate the interaction between microorganisms and coating surfaces and the impact of the biofilms formed by multiple species in the marine environment on MIC. Although a large number of studies have been reported on the development of the anti-MIC coatings, construction of the coatings with satisfactory performances still has a long way to go, since their toxicity, broad-spectrum antifouling activity, long-term service life, ease of fabrication and cost efficiency have to be taken into account simultaneously. Among the future work, fundamental research on the interaction at molecular level between the anti-MIC coatings and the microorganisms is to be investigated systematically. With the development of antifouling technology, a boom in the application of thermal-sprayed anti-MIC coatings is anticipated in the near future in response to the fast developing marine economy.

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