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Review

Sustainable antifouling coating technologies for the maritime industry: An evolutionary overview

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ABSTRACT

Biofouling of marine submerged structures due to the colonization of marine micro and macro-organisms continues to pose severe operational and ecological challenges. Traditional antifouling paints containing Tributyl Tin and Cybutryne were banned by the International Maritime Organization in 2008 and 2023 respectively due to their toxicity to marine ecosystem. Currently available antifouling paints fall into two broad categories: ablative or sloughing paints used for smaller vessels, and hard coat paints, such as vinyl and epoxy coatings, used for larger ships. Functionally, these coatings can be grouped into Foul release coatings, Protein resistant coatings, and the more recent Bioinspired coatings. This paper presents a consolidative review of modern antifouling coating technologies and their transition from conventional chemical formulations to advanced, biologically inspired and data-driven approaches. Eight major fabrication and surface engineering techniques, including deposition, templating, etching, electrostatic deposition, nanocomposite synthesis, additive manufacturing, micromachining, and self-assembly, have been discussed with reference to their antifouling mechanisms, benefits, and limitations. Special focus is given to laser-based micromachining methods, which enables precise modification of micro and nanoscale surface topographies. The review also explores the development of hybrid organic and inorganic coating systems, multifunctional and environmentally responsive materials, and the application of computational and machine learning tools for predictive design and accelerated testing of antifouling coatings. By combining these experimental and computational strategies, the study outlines a coherent direction for the creation of next generation coating systems that exhibit structural innovation, self-repairing capability, and intelligent performance. The paper concludes that collaborative research between laboratory scientists and the maritime industry will be essential for developing durable, effective, and environmentally sustainable antifouling solutions for future marine applications.

1. Introduction

In-spite of the ship's underwater hull being painted with marine antifouling protective coating, marine organisms' starts attaching itself to the ship's hull soon after the ship starts trading in the ocean. Bridge pillars, submerged legs of Oil rigs, Jetties and Pontoons, Cruise and Cargo ships and all other fixed or floating structures couldn't escape from the harmful effects of biofouling. Fig. 1 shows some recent pictures that reinstates the fact. Fig. 1(A) shows the hull of an oil/chemical tanker placed on the blocks during a scheduled drydock with visible biofouling. Fig. 1(B—C) shows severe colonization of bivalve Asian green mussels on hull of a dredger in the drydock, scheduled to ply on coastal waters.

These marine organisms come in various forms, shapes & sizes. Diatoms, Bacteria, Fungi, Protozoa, Algae, weeds, Molluscs, barnacles, mussels, chlorophytes [1] are some marine creatures that bind themselves with the hull, making antifouling coating ineffective. Considering a typical ocean-going Bulk Carrier of 50,000 tons deadweight, it's wetted surface area (the underwater area exposed to the sea) can range between 30,000 to 40,000 m^2 [2]. Colonization of these marine fouling organisms on the ship's underwater hull surface leads to an increase in underwater resistance, causing the ship to burn more fuel to maintain the same speed. Ship's speed can be reduced to 40 % due to hull fouling [3]. Fouling also leads to damage to the underwater paint and subsequent corrosion of the steel structure. Nevertheless, increase of greenhouse gas emission due to increased drag resistance is an unwanted effect.

Prior to 1st January 2003 ships were using Organotin compounds like TBT (Tributyl Tin) based antifouling coatings and self-polishing

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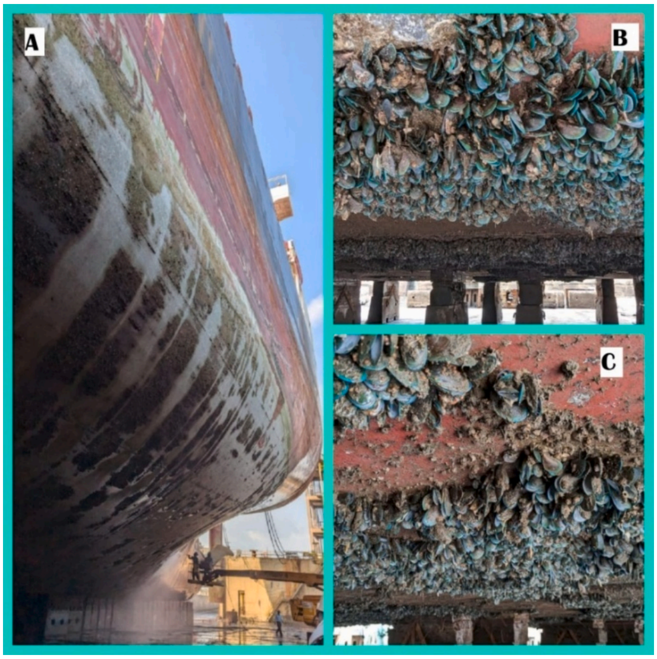

Fig. 1. Visible Hull fouling at drydocks (A) An oil/chemical tanker, (B)-(C) A Dredger on the blocks at drydock.

copolymers in which Tin, Mercury and Arsenic were used to deter fouling organisms from attaching themselves to the ship's hull [4]. But these harmful chemicals that were being released from the paint coatings were being absorbed by marine creatures [5]. They eventually passed into the food chain causing harm to humans as well. The International Maritime Organization (IMO) adopted the 'International Convention on the Control of Harmful Anti-fouling Systems on Ships' (AFS Convention) in October 2001, which banned the use of tributyltin (TBT) as antifouling paints.

While the convention was adopted in 2001, the ban on TBT-based antifouling paints became fully effective globally from 17th September 2008 [6]. Further to this in 2021, the Marine Environment Protection Committee (MEPC) of the IMO adopted amendments to include controls on the biocide Cybutryne. The amendments enter into force on 1 January 2023. This convention states that ships shall not apply or re-apply anti-fouling systems containing this biocide from 1 January 2023 [7].With these restrictions being imposed one after the other, it became an urgent necessity for the maritime community to find an alternative antifouling coating, which will be effective without harming the marine aquatic habitat. Ongoing research and technological developments have paved way for many emerging antifouling solutions. Recent developments involve utilizing natural biological substances as antifouling agents, or biomimetic coatings that imitate antifouling mechanisms observed in nature, including micro/nanostructured surfaces and slippery liquid-infused porous surfaces (SLIPS). Coatings based on polymers, particularly those formulated with amphiphilic, zwitterionic, or superhydrophilic polymers, have proven effective in preventing the attachment of proteins, bacteria, and larger organisms while reducing toxicity.

Nanocomposite coatings, which combine inorganic and organic hybrid materials, provide improved mechanical strength, superhydrophobic properties, and self-cleaning capabilities for enhanced durability. Integrated antifouling and anticorrosion coatings (IAACs) are gaining traction, as they merge various protective functions into a single layer to tackle both biofouling and material deterioration. Coatings that are multifunctional and self-healing, inspired by natural processes, are being researched to prolong service life and ensure performance in challenging marine environments. In summary, the current direction is toward more environmentally friendly and sustainable coatings that harness innovative solutions, advanced material science and bioinspired design to achieve high antifouling efficiency with minimal environmental impact.

This review aims to critically evaluate the recent technological developments in eco-friendly marine antifouling coatings, weighing their advantages and drawbacks. Prospective future research should address these limitations by incorporating the practical requirements of the maritime industry, which can pave the way for a broad-spectrum, widely acceptable, durable and economically viable antifouling system.

Clarksons estimated that the shipping industry emitted 845 million metric tons of CO_2 in 2022 (Clarksons' "Fueling Transition," April 2023). In the absence of biocidal antifouling coatings, biofouling on a vessel's hull and in various niche areas can lead to a fuel consumption increase of approximately 40 %. Based on Clarksons' 2022 emission estimate, this would result in an additional 338 million metric tons of CO_2 annually [8]. This pressing issue has driven the development of new coating technologies that align with the decarbonization targets of the International Maritime Organization (IMO). Effective coatings contribute to reduced fuel consumption and lower greenhouse gas emissions, thereby supporting IMO's vision for a more sustainable maritime sector.

ASTM has established several standards to evaluate the performance of marine antifouling coatings. ASTM D6903 assesses the release rate of organic biocides from antifouling coatings, ASTM D6442 determines the copper release rate, and ASTM D4939 evaluates coatings under biofouling and fluid shear forces in natural seawater. However, evaluations such as the Raft test and Hull test are time-consuming, based on prolonged observation, and are costly. To address this, certain hybrid testing methods have been suggested, simulating real-world marine environments in laboratory settings to enable faster evaluation [9], [10]. While several earlier research and reviews have examined antifouling coatings in general, most focused on chemical compositions, polymeric formulations, or biocide-free systems. The present study is distinct in that it consolidates eight major bioinspired surface-fabrication techniques, with an in-depth focus on micromachining and laser-based microstructuring methods. Unlike previous works, this review integrates surface engineering principles with biomimetic design strategies and evaluates their scalability, durability, and environmental sustainability for large-scale maritime applications [11].

This paper also synthesizes knowledge from marine biology, materials science, chemistry, and manufacturing engineering, providing researchers with a comprehensive, interdisciplinary understanding of the challenges and opportunities. By systematically outlining the various coating strategies, their fabrication methods, and their inherent limitations, the paper functions as a strategic roadmap. It guides future research toward synergistic, multi-functional systems and highlights the most pressing challenges that need to be solved to achieve commercial viability. This cross-disciplinary approach bridges the gap between laboratory research and industrial implementation, highlighting pathways toward next-generation eco-friendly antifouling coatings [12] [13].

2. Antifouling coatings

As of now, three major antifouling techniques are utilized in the industry: (1) Foul Release Coatings (FRC), (2) Protein Resistance Coatings (PRC), and (3) Bio-inspired Coatings [12]. These approaches employ various mechanisms such as the release of antifouling chemicals, specially textured surfaces, and low surface energy to prevent biofouling.

2.1. *Foul release coatings (FRC)*

Foul release coatings (FRC) operate by having a low surface energy that prevents organisms from forming a strong bond with the hull surface. The smooth texture of the coating at the molecular level ensures that fouling organisms are washed off once the vessel's speed reaches between 10 and 20 knots, depending on the marine fouling community present [14]. These non-stick surfaces facilitate the removal of fouling organisms by reducing the thermodynamic work required for adhesion. FRCs are versatile in their effectiveness against a variety of fouling organisms, but they do not prevent fouling while the vessel is stationary, at the dock or at anchor. These coatings are suitable for specific uses and do not necessitate the inclusion of classified environmentally harmful antifouling chemicals, making them a viable option for future application.

There are two main categories of FRCs: fluoropolymer and silicone-based polymer coatings. Typically, silicone coatings are applied at a dry film thickness (DFT) of 150 μm, whereas fluoropolymer coatings are generally 75 μm thick. The coating thickness allows for the adjustment of the coating modulus. A thicker coating, as observed with silicone elastomers, is more effective because it requires fewer foul release systems. [14], [15], [16]. Commercially available FRCs include International® Intersleek (AkzoNobel), Hempel's Hempasil X3, and PPG's Sigmaglide, all based on silicone or fluoropolymer technology that provide biocide-free fouling release through low surface energy [17].

2.2. Protein-resistant coatings (PRC)

Protein-resistant coatings (PRC), particularly those incorporating hydrophilic polymers or amphiphilic additives, have shown effectiveness in preventing protein adsorption and subsequent biofouling when used as underwater coatings on a ship's hull [18]. These coatings function through several key mechanisms. Hydrophilic surfaces reduce protein adsorption because proteins do not easily spread or denature on such surfaces; instead, they interact primarily through electrostatic forces [19]. Additionally, polymer coatings with high levels of hydration create a “stealth” effect, making the surface less attractive to protein molecules [20]. The hydrated nature and steric repulsion provided by hydrophilic polymers also prevent protein molecules from making close contact with the coated surface [21]. Amphiphilic additives, such as poly (sulfobetaine methacrylate)-polydimethylsiloxane [Poly (SBMA)-PDMS], can further enhance the fouling-release performance of hydrophobic coatings by encouraging the migration of hydrophilic components to the surface [22]. Despite these advantages, conventional PRCs tend to lose their effectiveness over time and are not reliable for long-term underwater use, which restricts their practical application in the marine industry [23]. Their declining performance in marine environment is due to a combination of various factors such as environmental degradation, surface damage, and the complex, multi-stage nature of marine biofouling [24] [25] [26] [27] [28].

Environmental degradation of protein-resistant coatings (PRCs) occurs through several mechanisms. Hydrophilic polymers such as polyethylene glycol (PEG), commonly used in PRCs, are susceptible to hydrolysis and oxidative degradation in seawater, particularly in the presence of transition metals, oxygen, and UV light. This results in the breakdown of chemical bonds and a loss of protein-repellent properties. Exposure to UV radiation and temperature cycling further accelerates deterioration, as sunlight induces photo-oxidation and chain scission in polymers, while temperature fluctuations cause expansion and contraction, leading to cracking and peeling of the coating. Additionally, wet-dry cycles in tidal zones promote salt crystallization within micro-defects, increasing surface roughness and damaging the coating structure. Surface damage and wear also play a major role in performance loss.

Mechanical damage from scratches, abrasions, and impacts caused by water movement or debris create defects that compromise the coating's protective function and serve as sites for organism attachment. Poor adhesion to substrates and microscopic pores formed during application or curing allow water and corrosive species to penetrate, resulting in delamination and corrosion. Furthermore, multi-stage marine biofouling contributes to the decline in effectiveness. Under static conditions, particularly for silicone-based PRCs, limited water movement fails to remove biofilms, allowing diverse microbial communities to adapt and degrade antifouling surfaces. As the coatings deteriorate, their surface chemistry changes, often becoming more conducive to protein and organism adhesion [29] [30].

While not yet common as commercial marine products, PRCs are often integrated as hydrophilic or zwitterionic polymer layers in advanced coating systems. Hydrogel based coatings and PEGylated surfaces are under development for commercial use, although marine-specific branded products are still in the early stages of emergence [17]. Referring to recent researches, we have witnessed some significant advances in materials and strategies for PRCs, with a focus on improving both durability and antifouling effectiveness. They are:

2.2.1. Zwitterionic and amphiphilic polymer coatings

Zwitterionic polymers such as poly (sulfobetaine methacrylate) and their nanocomposites have demonstrated strong protein resistance, high hydrophilicity, and excellent abrasion resistance. These coatings retain their antifouling performance even after prolonged exposure to seawater and repeated abrasion, and they can be applied to a wide range of substrates [31] [32]. Similarly, amphiphilic copolymers and layer-by-layer (LBL) coatings based on amphiphilic polysaccharides, such as alginate modified with hydrophobic groups, integrate both hydrophilic and hydrophobic domains. This dual character enhances protein resistance and mechanical durability, enabling these coatings to outperform purely hydrophilic or hydrophobic systems in preventing protein and microorganism adhesion [33] [34] [35].

2.2.2. Hybrid nanocomposites and bioinspired designs

Hybrid nanocomposite coatings that incorporate nanoparticles such as silica, cellulose nanocrystals, or heterostructures like MoS_2/MXene into polymer matrices offer enhanced mechanical strength, self-healing capability, and long-term antifouling performance. Some of these coatings are designed to mimic natural structures such as “brick and mortar” or “ridge-like” surfaces, which further minimize fouling and improve durability, with field tests demonstrating effectiveness for up to 180 days [36] [37]. Additionally, bottlebrush polymers and photoreactive copolymers have been developed to form thick, stable, and durable coatings that exhibit high resistance to protein adsorption and biofouling, maintaining their integrity even after several months of seawater exposure [38].

2.2.3. Synergistic and multifunctional approaches

Synergistic coatings integrate multiple mechanisms, including contact inhibition, fouling-repellent, and antifouling actions, to provide comprehensive protection against biofouling. These coatings have demonstrated the ability to resist protein, bacterial, and algal adhesion for over eight months in marine field tests [39] [40] [41] . Additionally, hydrogel-based and self-stratifying silicone coatings exhibit strong adhesion, slow degradation, and robust antifouling performance, making them well-suited for large-scale marine applications [42].

2.3. Bio-inspired antifouling coating

This strategy has drawn attention for research work since the inception of the term ‘Biomimetics’ in 1991. Bio-inspired antifouling coatings imitate nature, meaning strategies adopted by nature to combat fouling, and replicating them for industrial use. There are natural ways by which sharks, mussels, corals, lotus leaf are capable of resisting fouling on their skin and shell by a technique called microtexturing. These microtextures on the surface of sharks and mussels deter sea creatures like Algae, weeds, Molluscs, barnacles to colonize on their surfaces.

But bio-inspired micro-structured coatings also come with drawbacks. Some studies suggest that these colonizing sea organisms can gradually fill up the gap between these microstructures rendering these patterns ineffective [43]. Also, some microstructures are susceptible to damage even by gentle touch [44]. Commercial products in this category are at an early stage of development but include coatings that incorporate natural antifoulants e.g. Selektope® by I-Tech AB, which uses medetomidine, a compound inspired by natural defense mechanisms [17]. Selektope® used in very low concentrations in commercial paints (as little as 0.1-0.2 % by weight) significantly improves the coating's ability to remain clean even when a vessel is stationary, addressing a major weakness of some traditional antifouling systems.

Major paint manufacturers like Chugoku Marine Paints, Jotun, Hempel, and PPG offer commercial antifouling paint systems containing Selektope®. Various bioinspired antifouling coating strategies are studied in greater details in Section 4. Table 1 presents the key quantitative metrics for fouling-release coatings (FRCs), protein-resistant coatings (PRCs), and bio-inspired coatings, highlighting their comparative performance in terms of adhesion strength, surface energy, and durability.

Recent research and investigation on a sessile sea organism called Corals show some interesting facts. Corals are static living creatures and have a unique strategy to deter fouling on its surfaces. They use a combination strategy to deter marine aquatic species to attach onto themselves. (1) The first is the release of a bioactive antifoulant. (2) The second is low surface energy of the coral surface, which decreases surface adhesion strength, preventing organisms from attaching. (3) The third is the sloughing effect, in which they continuously excrete a slippery slime to remove attached organisms. (4) The fourth is the use of soft external tentacles that prevent organisms from attaching to their surface. (5) And fifth, the emission of weak fluorescent light that inhibits diatoms to colonize on their surface. Around 5800 types of chemicals have been isolated from Corals till now [23].

Various literatures have reported 52 varieties of corals and 188 compounds from them [58]. These compounds include sesquiterpenes, steroids, alkaloids, and diterpenes [59]. For example, cembrane diterpenes like 14-Deoxycrassin and sarcoglaucin-B [60] exhibit good potential to deter the attachment of fouling organisms and are known for their diverse ways to prevent fouling, namely excreting toxins, growth inhibition, interference of neural pathways, anti-adhesion quality and repellent action [61]. As mentioned earlier, a single antifouling chemical is not sufficient to keep all of the various bio-fouling creatures away [62]. Therefore, it has become necessary to include multiple chemicals in the antifouling coating to exhibit a broad-spectrum antifouling effect.

3. Surface properties governing antifouling coating performance

The performance of antifouling coatings relies on the surface properties of the coating material. Parameters such as wettability, sliding angle, surface energy, and hydrophilicity play a critical role in determining how effectively a surface can resist the attachment of fouling organisms. A fundamental understanding of these properties is essential for designing coatings that provide long-term protection in harsh marine environments.

3.1. Wettability

It refers to a surface's ability to interact with liquids and is commonly evaluated by measuring the contact angle between a water droplet and the solid surface [63]. This angle, known as the Young's contact angle (θe), is formed at the interface where solid, liquid, and gas phases meet, as illustrated in Fig. 2. A contact angle below ninety degrees typically indicates a hydrophilic surface, while angles above ninety degrees suggest hydrophobicity [64].

In context to antifouling coatings, increased hydrophobicity is often associated with better fouling resistance due to reduced surface adhesion of marine organisms. However, surface roughness also plays a significant role. On hydrophobic surfaces, increasing roughness results in a higher contact angle, making the surface more water-repellent. Conversely, on hydrophilic surfaces, increased roughness decreases the contact angle, enhancing water spread. These effects are described by the Wenzel and Cassie–Baxter models. According to the Wenzel model, the contact angle on a rough surface (θ_W) can be calculated using the relation $\mathrm{Cos}\ \theta_W = r\ \mathrm{Cos}\ \theta e$, where r represents the ratio of actual surface area (SA) to the projected area (SG) [23]. These models help researchers understand how micro- and nano-texturing of coating surfaces can amplify antifouling characteristics.

3.2. Sliding angle

It is another critical parameter that indicates how easily a water droplet can roll off a surface. It is defined as the angle at which a droplet begins to slide due to gravitational force acting on a tilted surface. As shown in Fig. 3, the sliding angle (β) is determined when gravity overcomes the adhesive force between the droplet and the surface, following the relation $mg \sin \beta = \gamma L\ W (\cos \theta_R - \cos \theta_A)$. In this equation, m is the mass of the droplet, g is gravitational acceleration, γL is the surface tension of water, W is the contact length of the droplet, and θ_A and θ_R are the advancing and receding contact angles, respectively. A lower sliding angle indicates better self-cleaning performance, which is a desirable trait for antifouling coatings because it allows fouling organisms and contaminants to be easily washed away by flowing water.

3.3. Lotus effect

It describes the phenomenon observed on certain natural surfaces, such as lotus leaves, where water droplets easily roll off due to a combination of low surface energy and hierarchical micro-nano surface structures [65]. This results in a low sliding angle and excellent self-

Table 1

Key quantitative metrics for FRCs, PRCs, and bio-inspired coatings.

Coating Type	Surface Energy (mJ/m^2)	Water Contact Angle (°)	Adhesion Strength (MPa)	Fouling Resistance Efficiency	Real-World Applicability	Citations
FRC: Silicone-based (PDMS), fluoropolymers	18.9-23	98-116	Less than 1.2	84-99 % removal of bacteria/diatoms	Widely used on commercial ships, offshore structures, and yachts; best for moving vessels; less effective during idle periods	[45] [46] [47] [48] [49]
PRC: Amphiphilic copolymers (PEG, PMMA, etc.), zwitterionic, hydrophilic/hydrophobic blends	20-30	90-110	1.2-3.3	80-98 % removal, especially with zwitterionic or amphiphilic additives	Increasingly used in marine and industrial settings; suitable for both static and dynamic conditions; scalable	[50] [51] [52] [53]
Bio-Inspired: Nanocomposites, hydrogels, biomimetic polymers, zwitterionic, polybenzoxazines.	18-24	116-133	2.0-5.4	98-99 % reduction in fouling, 84 % protein desorption	Emerging in marine, shipping, and industrial applications; promising for broad-spectrum antifouling and drag reduction	[54] [55] [56], [57]

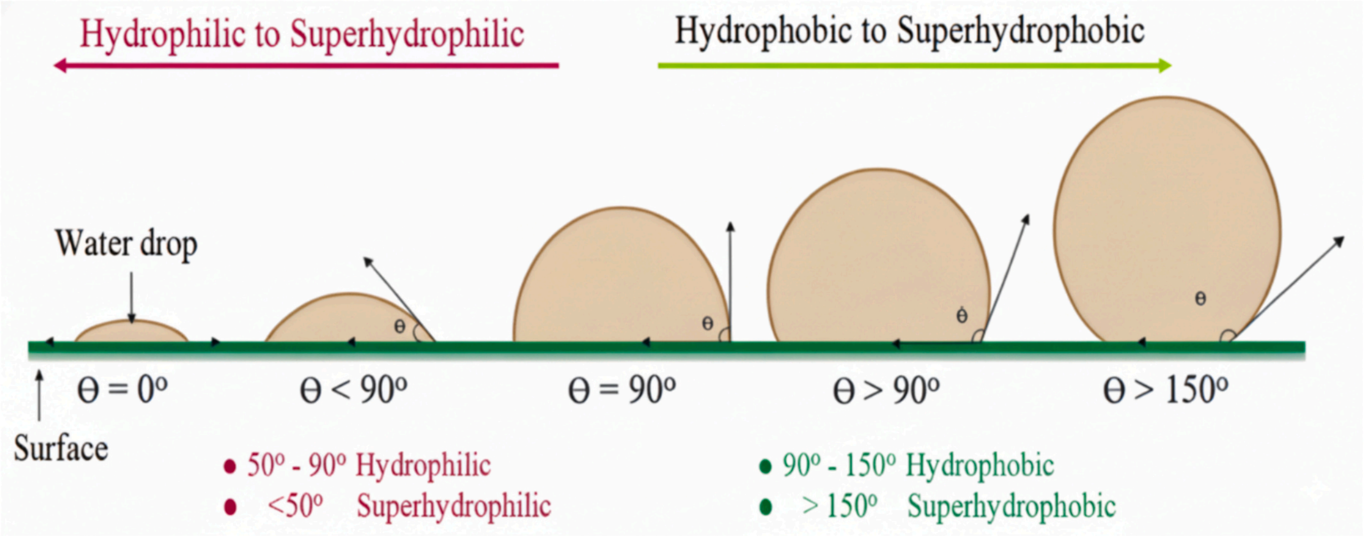

Fig. 2. Schematic diagram showing progression of contact angle from superhydrophilic to superhydrophobic.

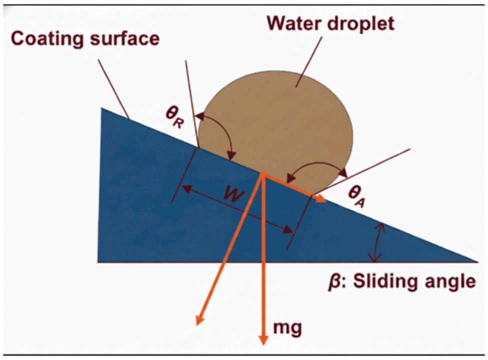

Fig. 3. Sliding angle β of a water droplet on a coated surface.

cleaning ability. When applied to antifouling coatings, replicating this effect can significantly reduce the attachment of pollutants and microorganisms, maintaining the surface cleanliness of marine vessels without the need for active biocides.

3.4. Petal effect

Rose petals exhibit super hydrophobicity as a result of their intrinsically water-repellent surface structure. However, water droplets strongly adhere to them despite their high contact angle [16]. This phenomenon indicates that not all superhydrophobic surfaces are self-cleaning. In antifouling applications, such strong adhesion would trap fouling organisms instead of repelling them. This highlights the importance of minimizing contact angle hysteresis to achieve effective self-cleaning surfaces, a key design parameter in modern fouling-release coatings.

3.5. Hydrophilic surfaces

Hydrophilic Surfaces offer an alternative approach to antifouling. Instead of repelling water like hydrophobic coatings, hydrophilic coatings form a tightly bound hydration layer when in contact with water. This hydration barrier creates steric repulsion, preventing proteins, bacteria, and other marine organisms from adhering to the surface. Due to their strong affinity for water, hydrophilic surfaces form a stable, uniform barrier that is difficult for organisms to penetrate. Materials such as polyethylene glycol (PEG), zwitterionic compounds, hydrogels, and hyperbranched polymers have shown promise in this area and are being actively researched for their fouling-resistant properties [58].

3.6. Surface energy

Surface Energy, also referred to as surface free energy or interfacial free energy, determines the ability of a surface to attract or bind surrounding molecules. A surface with high surface energy allows water to spread easily, promoting wetting, while a surface with low surface energy resists wetting and adhesion. In antifouling applications, low surface energy is advantageous because it makes it more difficult for fouling organisms to anchor to the surface. Contact angle measurement remains one of the most accessible methods for assessing surface energy [66]. The Baier curve, introduced by Robert E. Baier, provides a graphical correlation between surface energy and fouling rate. As depicted in Fig. 4, the optimal antifouling performance is typically achieved when the surface energy is between twenty-two and twenty-five milli newton per meter.

Hydrophobic marine antifouling coatings prevent organism adhesion primarily through a combination of surface roughness and low surface free energy, which together create physical and energetic barriers to

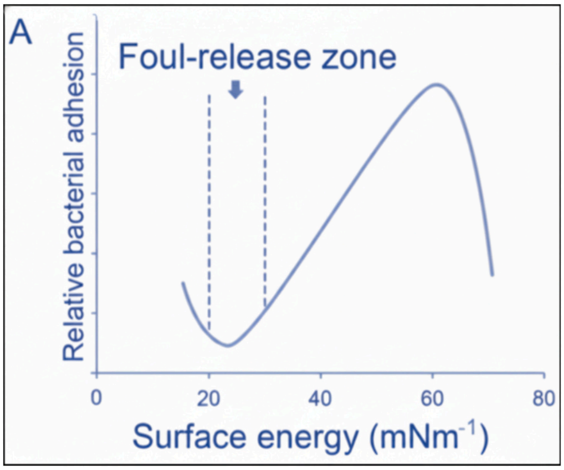

Fig. 4. Baier curve; the region between the blue dotted lines achieves maximum antifouling performance. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fouling. Surface roughness and air entrapment at the micro/nano scale enhance hydrophobicity by trapping air within surface grooves, as described by the Cassie-Baxter model. This reduces the actual contact area between water (and fouling organisms) and the solid surface, making it difficult for organisms to anchor. Superhydrophobic surfaces (contact angle $>150^{\circ}$) with engineered roughness show delayed fouling and minimal microorganism attachment in early immersion, as air pockets act as a barrier. However, excessive roughness can sometimes increase adhesion if it increases the effective surface area without sufficient air entrapment. So optimal roughness design is critical.

In an experimental study to investigate the behaviour of substrate surface roughness on the adhesion behaviour of Gram-negative as well as Gram-positive bacteria on a model hydrophobic surface (methylated quartz), the substrate roughness was varied from ~2 nm to ~390 nm. The combination of the surface roughness and methylation resulted in hydrophobic and superhydrophobic behaviour. By varying the surface roughness, a 75-fold variation in the number of adhering bacteria was observed during the experiment, demonstrating the importance of surface topography and the presence of entrapped air for effective antifouling. Both increased effective surface area with increasing roughness and decreased activation energy with increased surface roughness were found to increase the extent of bacterial adhesion. For the effectiveness of superhydrophobic surfaces, the amalgamation of factors included (a) the surpassing of Laplace pressure force of interstitial air over bacterial adhesive force, (b) the reduced effective substrate area due to air gaps for the bacteria to have direct contact, and (c) the reduction of the attractive van der Waals force that holds adhering bacteria on the substrate (the energy barrier of bacterial desorption/removal) [67].

Low Surface Free Energy (SFE) materials, such as silicone and fluoropolymers, minimize the thermodynamic driving force for adhesion. Organisms find it energetically unfavourable to attach, as the adhesive bond strength is weak. Coatings with SFE ~ 22 mJ/m^2 are especially effective, as evidenced by dramatic reductions in bacterial and algal adhesion. The combination of low SFE and roughness leads to high water contact angles and minimal protein, bacterial, and algal attachment [55]. The combination of surface roughness and low surface free energy (SFE) results in self-cleaning, fouling-release surfaces, where weakly attached organisms can be easily removed by turbulent water flow or gravity. Biomimetic and nanocomposite coatings further enhance these effects, offering long-term durability and resistance to both micro- and macrofouling [68].

Among materials exhibiting low surface energy, polydimethylsiloxane (PDMS) has gained considerable attention for its antifouling potential. PDMS coatings, through chemical modifications, can create stable interfaces that resist microbial colonization and the attachment of particulates [16]. These hydrophobic PDMS-based coatings also offer self-healing properties by incorporating dynamic covalent bonds within polymer chains, allowing them to repair minor surface damage. Their advantages include good flexibility, elastomeric behaviour, thermal stability, and optical clarity.

However, limitations such as low mechanical strength, weak adhesion, high cost, and limited antifouling performance in static conditions hinder their wide-scale adoption [69]. To address these drawbacks, Liu et al. [70] developed a novel PDMS-based antifouling coating (PDMS-Pun-X) that mimics the natural antifouling strategies used by carps. This coating combines the controlled release of eugenol with low surface energy characteristics to deliver both self-regulating and self-healing antifouling properties, representing a promising advancement in the field.

4. Novel marine antifouling coatings inspired by nature

Marine structures such as offshore oil rigs, floating platforms, seafaring vessels, and bridge piers are persistently exposed to the challenges of marine biofouling. No single antifouling strategy has been found to offer comprehensive protection against the diverse range of fouling organisms. As a result, a multifunctional approach has become essential. Such strategies may include (a) combinations of various bioinspired mechanisms or (b) hybrid systems integrating both bioinspired and conventional (non-bioinspired) techniques. These composite approaches aim to enhance the effectiveness, reliability, and longevity of antifouling coatings in real-world conditions.

Numerous plants and animals in nature employ specialized strategies to resist biofouling. Inspired by these natural mechanisms, the maritime industry has developed coatings that emulate the antifouling properties observed in biological systems. A schematic overview of six prominent bioinspired strategies is presented in Fig. 5. These strategies can be broadly classified into six categories [16].

4.1. *Micro/nanostructured surface*

Certain natural surfaces such as lotus leaves, dahlia petals, rice leaves, and shark skin exhibit micro- or nanostructures that effectively deter the adhesion of fouling organisms. These structures reduce contact points between the surface and fouling agents. As illustrated in Fig. 6 through SEM images, the lotus leaf serves as a classic example wherein surface microstructures trap air between water droplets and the leaf surface. Additionally, epicuticular wax secreted by the leaf surface contribute to its hydrophobic nature. The combined effect results in a superhydrophobic, low-adhesion surface that not only prevents fouling but also exhibits self-cleaning behaviour [71] [1]. A nanocomposite superhydrophobic coating was fabricated via a simple sol-gel synthesis method in a recent experiment using naturally sourced nanomaterials like cellulose nanocrystals (CNCs) as nanofillers. The synthesized coating developed a biomimetic microscopic ridge-like surface, where more CNCs contents accommodated to form finer microstructures.

During a 90 days marine field trial, CNC20 demonstrated good antifouling ability, proposing itself as an efficient microstructured AF coating [72]. Though not a marine product, it may be worthwhile to mention that Sharklet Technologies, Inc. commercially produces adhesive films and surfaces for areas which are frequently touched or are prone to bacterial infection (e.g. door handles, counter tabletops, washrooms). The produced surfaces mimic the microtopography of a sharkskin, thus repelling colonization of germs and bacteria [73]. Finsulate® in the Netherlands is another production company manufacturing microstructured films for underwater surfaces of yatches and boats [74]. These films for the underwater surfaces resemble the spines of sea urchins, which deters biofouling.

4.2. *Natural antifoulant secretion*

Corals deploy chemical-based antifouling strategies. Approximately 188 bioactive compounds have been identified from 52 coral species, each playing a role in deterring settlement and growth of marine foulants [23]. These natural secretions offer potential prototypes for synthetic antifouling formulations. In a recent experimental study, the fouling inhibition property of a naturally occurring marine non-toxic antifoulant Chlorogentisyl alcohol (3-chloro-2,5-dihydroxybenzyl alcohol, CHBA) was utilized to create a composite coating. The coating was prepared by combining silicone-modified polyurethane (SiPU) and CHBA. CHBA empowered the composite coating with static marine AF performance, while SiPU provided dynamic AF ability. This composite coating demonstrated anti-protein adsorption and algal inhibition capability for up to 90 days in seawater [76].

A natural AF chemical in commercial use is Selektope®. The product Selektope® by I-Tech AB has medetomidine (used as sedative in medical science) as the active ingredient. Major paint manufacturers like Chugoku Marine Paints, Jotun, Hempel, and PPG offer commercial antifouling paint systems containing Selektope® [77]. They infuse this chemical in their epoxy paints to achieve better AF properties [78]. In another interesting experimental study 'Eugenol' was incorporated into self-polishing polymers (like eugenol methacrylate), whereby eugenol

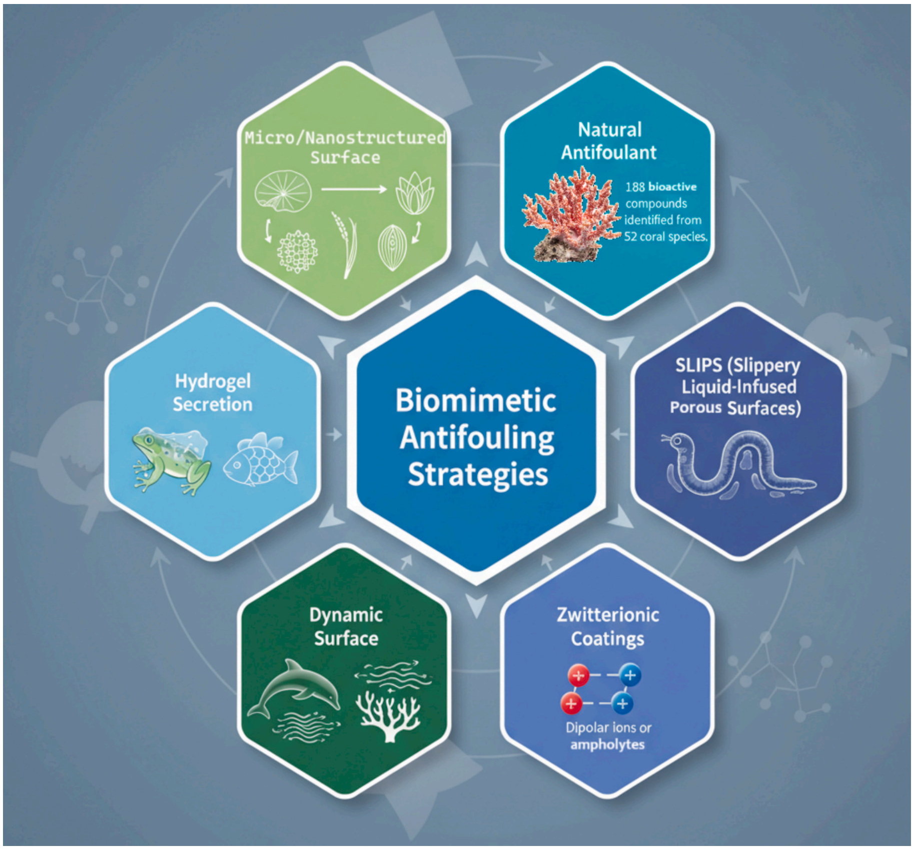

Fig. 5. The Six different bioinspired antifouling strategies utilized by nature.

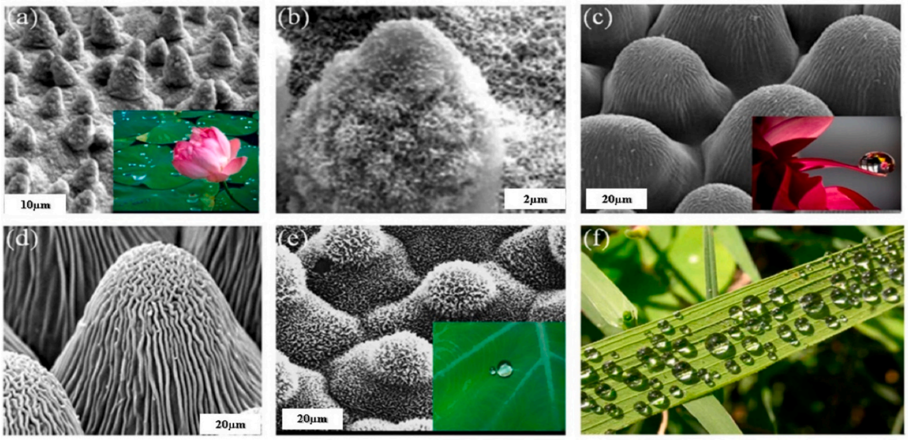

Fig. 6. **(a)** SEM 10 μm image of a lotus leaf (inset showing water droplets on the lotus leaf), **(b)** 2 μm magnification image of lotus leaf illustrating the hierarchical structures, **(c)** SEM 20 μm image of cuticles on the papillae of a Dahlia (inset showing a droplet on dahlia petal), **(d)** SEM 20 μm image of cuticles on papillae of rose petal, **(e)** Epicuticular wax crystals over the taro leaf (inset depicting superhydrophobocity of the droplet over the leaf), **(f)** Water droplets over the rice leaf proving its superhydrophobicity [75]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

was released in a controlled manner. As the coating slowly hydrolyses in seawater, it releases eugenol, continuously refreshing the antifouling effect over time [79]. These commercial and near-commercial antifoulants holds promising prospectives as marine eco-friendly coatings.

4.3. *Mucus-based surface protection*

Fish and certain amphibians possess skin or scales that secrete a mucous layer. This mucus forms a slippery barrier that reduces surface adhesion of fouling organisms. For instance, the scales of fish and the skin of frogs continuously secrete mucus, creating a hydrated, lubricated surface that impedes fouling to a considerable extent [80]. However, these low surface energy coatings require turbulence to wash-off foulants, thus getting ineffective when the submerged structure is stationary. In an experimental study to mimic the soft mucus-covered skin of a squid, stable polyvinylpyrrolidone (PVP) hydrophilic sections were introduced to modify the polydimethylsiloxane-based polyurethane (PDMS-PU), producing low surface energy elastomer coatings with hydrophilized defensive surface and reduced elastic modulus.

The surface was tested for performance in marine water for 150 days.

Results exhibited good antifouling performance, and improved anti-adsorption capability on biological proteins, bacteria and algae. Outcome of this experiment can pave the way for more efficient elastomer based commercial AF marine coatings [81].

4.4. *Slippery liquid-infused porous surfaces (SLIPS)*

SLIPS are engineered by infusing a lubricating liquid into a porous microstructured surface. This concept is inspired by organisms like earthworms, which possess microstructures covered with a stable liquid layer. The liquid remains locked within the surface due to capillary forces, resulting in a smooth, non-stick surface that offers superior resistance to biofouling colonization [82]. However, the reduction in antifouling performance caused by lubricant loss limits their application as marine AF coating. Research work is in progress to address this issue. Inspired by hagfish's defensive behaviour by secreting mucus, a smart SLIPS marine AF coating was prepared possessing responsive self-replenishment of lubricant, and self-adjusting surface lubricity between “enhanced” and “normal” modes. The prepared AF surface exhibited efficient self-cleaning, anti-protein, antibacterial, anti-algae properties in a 180 days marine field test [83]. In another similar experimental study, poison dart frog defensive and offensive technique was mimicked to create a new type of SLIPS, the Slippery Porous-liquid-Infused Porous Surface (SPIPS). The resultant SPIPS demonstrated lubricant self-replenishment, self-cleaning, anti-protein, anti-bacterial, anti-algal, and self-healing properties during a 360-day antifouling performance test [84]. These experimental results may illuminate newer horizons for commercial SLIPS based AF coatings.

4.5. *Dynamic surfaces*

Dynamic surfaces resist fouling through continuous renewal or structural instability. Crustose coralline algae, for example, periodically shed their epithelial layers to eliminate attached biofilms and foulants. Dolphin skin, characterized by its soft and elastic properties, also exemplifies a dynamic surface that actively resists biofouling in turbulent marine environments [85]. Macrophage is a type of white blood cell that surrounds and kills microorganisms by releasing free radicals. This inspiration was utilized in an experiment to formulate marine AF coating by incorporating dimethylglyoxime (PU_x-DMG) in polyurethane.

PU_x-DMG was prepared by precise regulation of dynamic oxime-urethane covalent bonds. The obtained alkyl radical (R·) derived from the cleavage of the oxime-urethane bonds effectively suppressed the adhesion of marine biofouling. Moreover, the intrinsic dynamic surface made it difficult for biofouling to adhere to the substrate. During a 4 months sea trial, the PU_{50}-DMG coating demonstrated repulsion to bacterial and algae, and also prevented macroorganisms from settling on the substrate [86]. In another experimental research, controlled-release boron-polyurethane antifouling coatings (DBIT) was prepared as a micro-dynamic surface. 2, 2-bis(hydroxymethyl)propionic acid (DMPA) was used as the reaction site and pyridine-diphenylborane (PDB) as the AF functional side chain groups, thus providing the coatings with the controlled release ability. In a 4 months field test, the $DBIT_{75}$ coating exhibited reduced settlement of Halamphora sp., *Nitzschia closterium*, and repelled settlement of mussels [87]. These results show that controlled dynamic surface coatings can be good choice as commercial AF coatings.

4.6. *Zwitterionic coating*

Zwitterionic compounds, also known as dipolar ions or ampholytes, contain both positive and negative charges within the same molecular structure, resulting in an overall neutral charge. These materials are recognized for their exceptional antifouling performance, primarily due to two mechanisms: high surface hydration and electrostatic repulsion. Their ability to form strong hydration layers repel charged foulants, making them ideal candidates for marine coatings. The term “Zwitter” originates from the German word for “hybrid.” The architecture of zwitterionic molecules typically involves alternating charged groups along polymer chains, which facilitates the formation of a stable hydration layer that deters biological adhesion.

The earliest inspirations for zwitterionic coatings emerged from medical applications, where polyethylene glycol (PEG) is commonly used to prevent fouling on medical implants. PEG is a soft, biocompatible polymer that forms a hydration layer via hydrogen bonding, thereby resisting protein adsorption and microbial adhesion. Recently, PEG-based coatings have been explored for marine applications, including ship hulls. Another promising zwitterionic polymer, poly (sulfobetaine methacrylate), attracts a layer of water molecules to its surface, effectively forming a hydration barrier that hinders foulant attachment [15] [88].

Getting inspirated from the smooth, mucous covered skin of the Lionfish, an experimental study integrated zwitterionic segments with hydration-based fouling-release properties of the Furan Oxime Ester structure having intrinsic antibacterial activity. This led to the development of a silicone-based antifouling coating capable of being functional from shallow to deep-sea environments. Field panel immersion tests confirmed this coating's effectiveness to deter the adhesion of larger shallow-water fouling organisms. Also, after immersion at a depth of 7730 m in the Mariana Trench for 51 days, no live bacteria are detected on the coating surface [89]. Another experimental study created a durable, paintable and scalable AF coating with zwitterionic hydrogel (PSDA-Z) covalently attached to substrates through an Acrylated Epoxy Resin Primer coat. This coating sustained its AF performance after 3 months of high-speed water shearing, high-pressure sandpaper abrasion, and sharp scratching [90]. These experimental coatings can emerge as forerunners in the field of commercial bio-inspired AF coatings.

4.6.1. *Antifouling mechanism of zwitterionic coatings*

4.6.1.1. Surface hydration. Zwitterionic compounds attract and retain water molecules due to their charged groups, resulting in the formation of a thick hydration layer. This layer serves as a physical and energetic barrier, preventing the adhesion of proteins, cells, and microorganisms [91].

4.6.1.2. Electrostatic repulsion. The intrinsic presence of both positive and negative charges on zwitterionic surfaces generates an electrostatic field that repels similarly charged foulants. An example of this mechanism is observed in the phosphatidylcholine groups found in biological lipid bilayers, which resist fouling through a combination of electrostatic and hydration forces [16].

Despite their potential, zwitterionic coatings also pose challenges. Their hydrophilic and often soft, porous nature makes them susceptible to the accumulation of marine sediments and inorganic particles, thereby reducing their antifouling efficacy over time in real-world conditions [92].

Moreover, the strong hydrophilicity of zwitterionic materials can hinder their adhesion to hydrophobic substrates, limiting practical application and durability [93]. Certain zwitterionic monomers, such as sulfobetaine methacrylate (SBMA), may not significantly outperform existing alternatives in fouling-release performance. The antifouling efficiency largely depends on the specific zwitterion used and its concentration in the coating formulation [94]. To address these limitations, researchers are exploring amphiphilic coatings that integrate zwitterionic and hydrophobic domains. Such systems offer improved resistance to both biofouling and sediment accumulation but introduce greater complexity in synthesis and design [95], [96]. While zwitterionic coatings are generally considered environmentally benign and offer a promising alternative to toxic organotin-based paints like TBT, ongoing research is necessary to optimize their mechanical strength, environmental stability, and long-term performance under marine conditions [93].

These bioinspired strategies collectively provide an environmentally sustainable pathway for antifouling coatings, avoiding the adverse ecological impacts of conventional toxic paints and holding considerable promise for future marine applications.

4.7. Challenges and future directions in bio-inspired marine AF coatings

4.7.1. Fundamental challenges

4.7.1.1. Durability and mechanical integrity. Bio-inspired coatings often emphasize on surface functionality (e.g., hydrophobicity, lubricity) at the expense of mechanical robustness. For example, hydrogel-based coatings exhibit good foul-release properties but suffer from poor abrasion resistance and delamination under hydrodynamic stress [97] [98]. The compromise between flexibility (for fouling release) and stiffness (for durability) requires attention. Metal-organic framework (MOF) coatings, inspired by nacre's “brick-and-mortar” structure, improves strength but face challenges in interfacial bonding under marine conditions [99] [100].

4.7.1.2. Environmental and ecological safety. While bio-inspired coatings aim to replace toxic biocides (e.g. tributyltin, Chlorothalonil, Dichlofluanid, Sea-Nine 211, Diuron, Irgarol 1051 and Zinc Pyrithione), some still incorporate heavy metals (e.g., copper, zinc) or synthetic polymers with slow degradation rates. Leaching of these components can harm non-target marine organisms and accumulate in ecosystems [101] [102]. Natural antifoulants like capsaicin analogues or plant extracts exhibit lower toxicity but suffer from rapid leaching and instability in seawater [103] [104].

4.7.1.3. Broad-Spectrum efficacy. Marine fouling involves diverse organisms (bacteria, algae, barnacles), each requiring a different defense mechanism. Bio-inspired strategies often target specific fouling types: Cell-membrane mimetic surfaces repel bacteria but fail against macrofoulants like mussels [105]. Superhydrophobic coatings deter initial biofilm formation but lose effectiveness when microscopic defects trap organic matter [106]. This lack of universality necessitates complex multi-strategy formulation, increasing fabrication complexity [107].

4.7.1.4. Scalability and manufacturing. Imitating natural micro/nanostructures (e.g., shark-skin denticles, lotus-leaf textures) requires advanced techniques like nanoimprinting, layer-by-layer assembly or micromachining. These processes are cost-prohibitive for large-scale applications like ship hulls [108] [109]. For example, PDMS-based coatings with microtextures face challenges in uniform application on curved, intricate, hard to access surfaces [110].

4.7.2. Key innovations and evolving strategies

Recent advancements in antifouling coatings emphasize multifunctionality, adaptability, and biomimetic design to enhance performance and environmental compatibility. Multifunctional and self-healing systems integrate antifouling properties with corrosion resistance and autonomous repair. For instance, self-healing polyurethane/imidazole composites containing disulfide bonds can regenerate after mechanical damage, thereby reducing maintenance requirements [111]. Similarly, metal-organic framework (MOF)-enhanced coatings such as ZIF-8@SiO_2 combine fouling resistance with passive anti-corrosion capabilities, mimicking the layered structure of natural nacre [112]. Although these systems address major durability gaps, further optimization is necessary to ensure their long-term stability under continuous seawater exposure.

Dynamic and stimuli-responsive coatings represent another emerging strategy, capable of adapting to environmental cues. Light-activated systems incorporating fluorescent phosphors (e.g., SWLAP/PDMS) store solar energy during the day and emit light at night, deterring diatom settlement [113] [114]. Similarly, pH- and temperature-responsive hydrogels can swell or shrink in response to environmental fluctuations, facilitating the detachment of fouling organisms by mimicking the natural defense mechanisms of marine mucus. [115].

Despite their promise, the reliability of these adaptive systems under variable marine conditions such as turbidity, temperature shifts and salt crystallization requires long-term field validation. A parallel line of innovation involves biomimetic hierarchical design inspired by natural antifouling mechanisms. Goose-feather-inspired superhydrophobic surfaces utilize biomass-derived carbon to achieve dual-scale roughness, resulting in high water contact angles and a 95 % reduction in bacterial adhesion [116]. Similarly, pitcher plant-inspired lubricant-infused slippery surfaces employ infused oils that form a mobile lubricating layer capable of continuously shedding fouling organisms [117]. Together, these strategies highlight the transition toward intelligent, nature-inspired surface systems that combine physical, chemical, and biological resilience for sustainable antifouling performance.

4.7.3. Future research trajectories

Future bioinspired AF coating research must increasingly prioritize sustainability through cradle-to-cradle design principles, such as replacing petrochemical polymers with algae-derived resins and developing in-situ degradation monitoring systems (e.g., fluorescent tagging) to evaluate environmental impact [118] [119]. Artificial intelligence and computational modelling can play a pivotal role in optimizing hierarchical surface architectures by simulating marine organism interactions and predicting fouling behaviour. For instance, neural network-based models can estimate barnacle adhesion on textured surfaces, while multi-scale fluid-coating interaction studies can guide the design of hydrodynamically efficient fouling-release materials [120] [121].

Advances in smart manufacturing are equally significant, with three-dimensional printed bio-templates enabling large-scale replication of biomimetic micro- and nano-textures such as coral spines through micromachining and additive manufacturing. Complementarily, nanocontainer technology employs microcapsules to deliver non-toxic antifoulants such as enzymes that are released in response to biofilm-associated biochemical triggers [122]. Together, these innovations represent a new generation of environmentally adaptive antifouling strategies that integrate structural and chemical responsiveness. Furthermore, the long-term performance of such materials requires rigorous field-validated longevity studies extending beyond laboratory conditions. Extended real-sea trials over 36-60 months, corresponding to vessel dry-docking intervals, across diverse biogeographic zones are critical to assess coating durability, ecological compatibility, and fouling resistance [123].

4.7.4. Integration with broader sustainability goals

Bio-inspired antifouling coatings must align with the IMO's 2030 emissions targets by reducing ship's greenhouse gas emission. Collaborative frameworks linking materials science, marine biology, and regulatory policy are essential to accelerate adoption. Bio-inspired marine AF coatings represent a paradigm shift from toxic biocides to ecologically harmonized solutions. Overcoming challenges like mechanical fragility, scalability, and organism-specific efficacy requires interdisciplinary innovation. Future success pivots on sustainable materials, smart responsiveness, and industrial-academic partnerships to transform laboratory breakthroughs into seaworthy technologies.

5. Manufacturing techniques for the industrial scale production of environmentally friendly antifouling surfaces and coatings

Advancements in technology have enabled the development of diverse techniques for fabricating micro- and nanostructured surfaces tailored for environmentally friendly antifouling applications. These techniques include deposition methods, templating (or soft lithography), etching, electrostatic deposition, nanocomposite fabrication, additive manufacturing (3D printing), micromachining, and self-assembly approaches [16]. A graphical representation of these techniques is provided in Fig. 7. Each technique plays a vital role in developing functional and scalable antifouling surfaces. The subsequent subsections elaborate on these techniques individually. (See Figs. 8 and 9.)

5.1. Deposition

The fabrication of textured surfaces through deposition primarily involves three major methods: Layer-by-Layer (LBL) deposition, Electrodeposition, and Chemical Vapor Deposition (CVD).

5.1.1. Layer-by-layer (LBL) deposition

LBL deposition involves the sequential adsorption of oppositely charged polyelectrolytes onto a substrate, resulting in a multilayered micro/nanostructured surface. This technique is robust, relatively simple, and can be employed over large surface areas to generate rough textures suitable for antifouling applications. However, creating highly undulated or complex microstructures requires the deposition of multiple layers, making the process labor-intensive and time-consuming [124]. Also, LBL coatings have inadequate long-term stability due to hydrolysis of polyelectrolyte bonds in seawater [125]. Moreover, the use of pH-sensitive or weakly bonded linkages in some LBL coatings may lead to detachment of the outer layers under varying environmental conditions, thereby compromising long-term effectiveness [126].

Potential areas of improvement are development of Covalent Cross-Linking polymers, i.e. integrating photo-crosslinkable polymers (e.g., diazirine derivatives) to enhance interlayer adhesion and hydrolytic resistance [127]. Another proposed enhancement is nanocontainer integration, which involves embedding pH-responsive nano capsules for the controlled release of biocides, thereby reducing environmental toxicity [128].

5.1.2. Electro deposition

Electrodeposition is a well-established technique where two oppositely charged electrodes are immersed in an electrolyte solution. Upon applying a current, metal ions from the anode dissolve and are deposited as a coating onto the cathode. By adjusting the process parameters, the texture and topography of the deposited layer can be precisely controlled. This technique is applicable to metals, composites, and polymers, and is widely used for generating micro- and nanostructures [65]. However, electrodeposited structures often suffer from low durability, mechanical fragility, and weak adhesion to the substrate [129].

Long-term performance in marine environments may be hindered by issues such as swelling, delamination, and degradation, especially if the coating or substrate is inadequately prepared. Additionally, the process is limited to conductive substrates, restricting its applicability. Environmental factors such as pH, temperature, and electrolyte composition can further influence reproducibility and coating quality [130].

Improvements to address the limitations of this method include the use of pulse electrodeposition, where optimizing the pulse frequency can achieve nanocrystalline coatings, such as Ni-Zn-P alloys, with 40 % higher hardness and superior corrosion resistance [131]. Additionally,

Fig. 7. Eight antifouling coating manufacturing novel techniques.

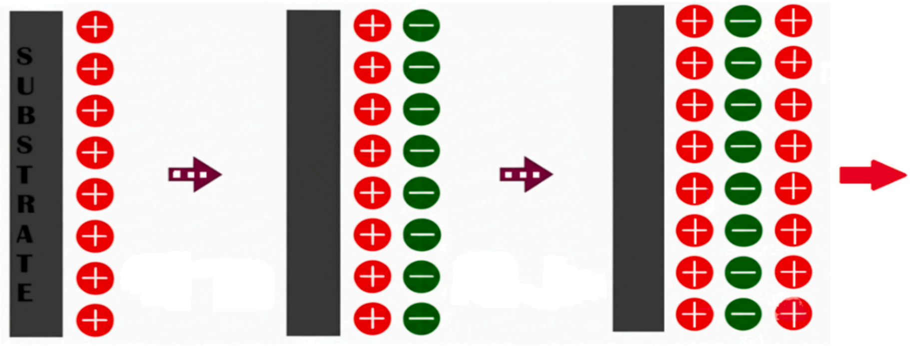

Fig. 8. Schematic diagram explaining LBL technology.

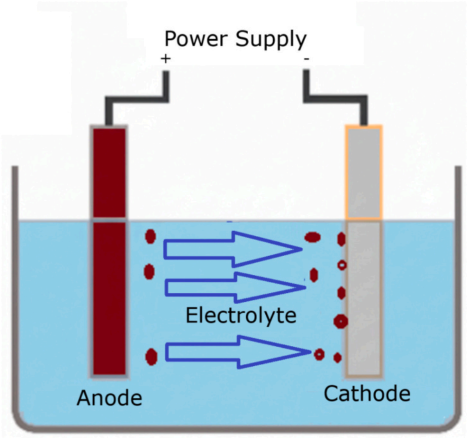

Fig. 9. Schematic diagram explaining Electrodeposition.

the development of hybrid composites by co-depositing graphene oxide nanoparticles can enhance barrier properties and reduce porosity [132].

5.1.3. Chemical vapor deposition (CVD)

CVD is extensively utilized for depositing thin films of nanostructures onto solid substrates. There are two common variants: Initiated CVD (iCVD) and Plasma-Enhanced CVD (PECVD). These solvent-free techniques are effective for producing thin, dense antifouling coatings on a broad range of substrates [133]. CVD offers precise control over coating thickness, composition, and surface functionality, enabling the fabrication of ultrathin, durable, and functional layers incorporating zwitterionic, hydrophilic, or fluorinated polymers. These coatings exhibit excellent resistance to protein, bacterial, and biofilm adhesion.

A schematic of the PECVD setup is shown in Fig. 10, where surface modification of a polysulfone (PSf) flat sheet membrane is illustrated. PECVD address the problem of thermal distortion of the polymer substrate by enabling lower deposition temperatures (≤100 °C), making it suitable for applying fluoropolymer coatings on thermoplastic substrates. The experimental setup consists of a cylindrical quartz vacuum chamber encircled by a copper coil antenna that generates high-frequency radio waves, serving as a plasma generator. The PSf membrane is mounted on flat silicon wafers and placed inside the vacuum chamber. A vacuum pump evacuates the chamber, while the monomer, vaporized in a stainless-steel container, is introduced via a precision metering valve.

A cooling plate regulates the substrate temperature, ensuring controlled deposition. The desired surface morphology is achieved as gaseous ions accumulate on the substrate. Adjusting various parameters allows for tuning of the resulting nanostructure. Despite its advantages, the CVD process presents certain limitations. The use of toxic and flammable gases poses safety risks, potentially hindering large-scale industrial adoption [134].

Additionally, multi-component deposition remains challenging due to varying vaporization rates among different precursors. The process also demands sophisticated and expensive equipment, along with stringent control of operational parameters, which limits scalability and increases production costs [135]. While CVD delivers high performance

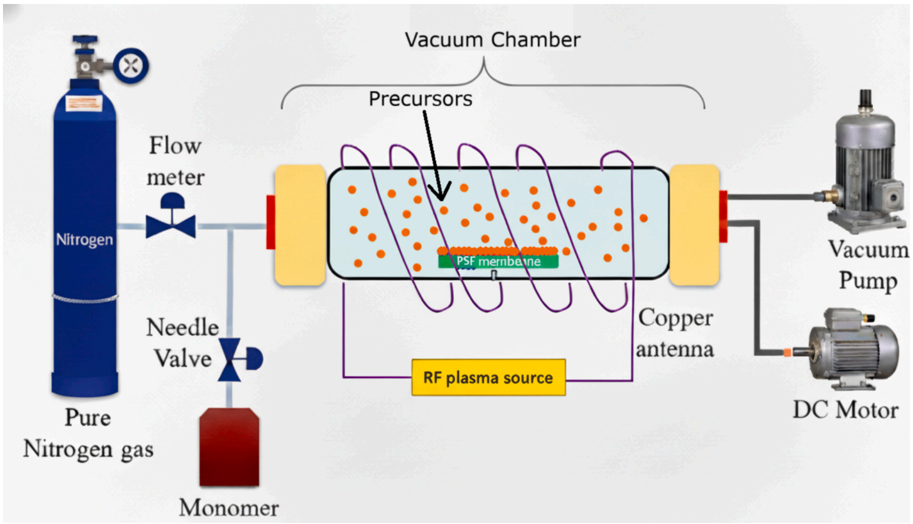

Fig. 10. Schematic drawing of PECVD process.

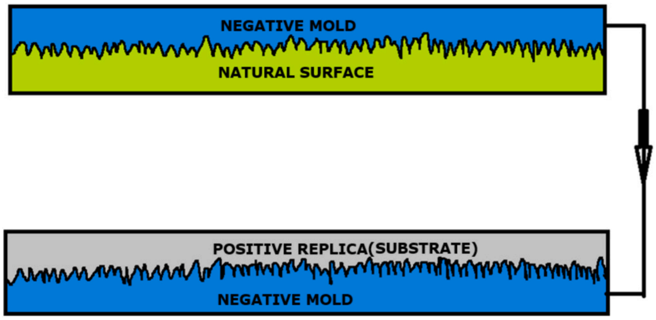

Fig. 11. Schematic drawing explaining the process of templating.

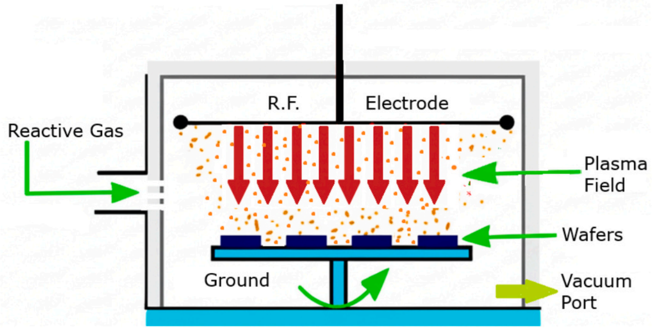

Fig. 12. Dry etching (plasma etching) process.

and versatility for antifouling coatings, practical implementation on large or irregular surfaces continues to be constrained by these precisely controlled technical factors as also high energy consumption [133]. An area of improvement to address the drawbacks of this process is Area-Selective CVD, using atomic layer masking, allowing for the patterning of hydrophobic and hydrophilic domains, leveraging bio-inspired topology [136].

5.2. *Templating or soft lithography*

Templating, also known as soft lithography, is a biomimetic manufacturing technique used to replicate the surface textures of naturally occurring antifouling surfaces. The process typically involves two key steps: the formation of a negative mold that captures the intricate surface features of a natural template, followed by the fabrication of a positive replica from the mold. A visual representation of the soft lithography process is provided in Fig. 11. Depending on the intended substrate material, desired resolution, and production scale, several techniques can be employed within the templating approach. These include casting, injection molding, microcontact printing, nano-imprint lithography, and embossing [16].

These methods are compatible with a wide range of materials and, importantly, can be adapted for large-scale manufacturing through roll-to-roll processing, enabling continuous production of antifouling surface textures over extended areas [137], [138]. Despite its advantages, the templating technique presents certain limitations. Achieving uniform and defect-free patterning across large surface areas or highly curved geometries can be challenging. Additionally, there is a risk of pattern collapse or deformation, particularly when working with high-aspect-ratio features or flexible substrates.

To address these challenges, recent advancements have incorporated CNC machining [139], chemical etching [140] and electroplating [141] for the precise fabrication of robust negative molds. These modifications aim to improve replication fidelity and reduce pattern defects. Other proposed improvements focus on techniques like Breath-Figure Templating, which generates hierarchical honeycomb structures through controlled condensation, allowing for tunable pore sizes ranging from 100 nm to 10 μm [142]. Another upcoming development is the formation of self-healing molds (silicone molds) with dynamic disulfide bonds, promising to extend template lifespan five-fold [143].

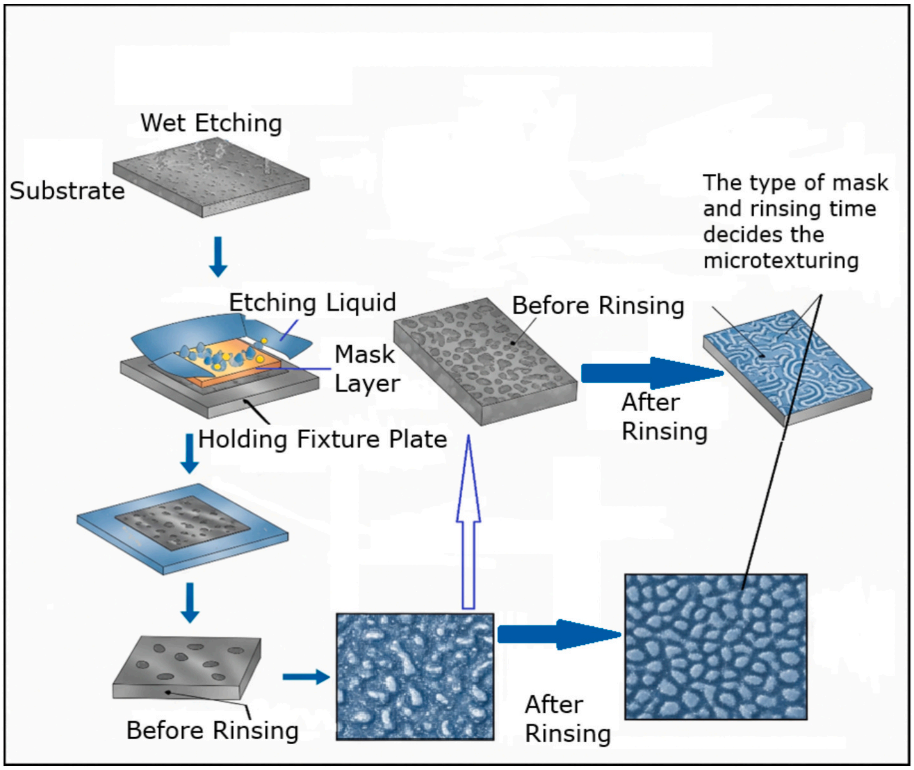

Fig. 13. Wet/chemical etching process.

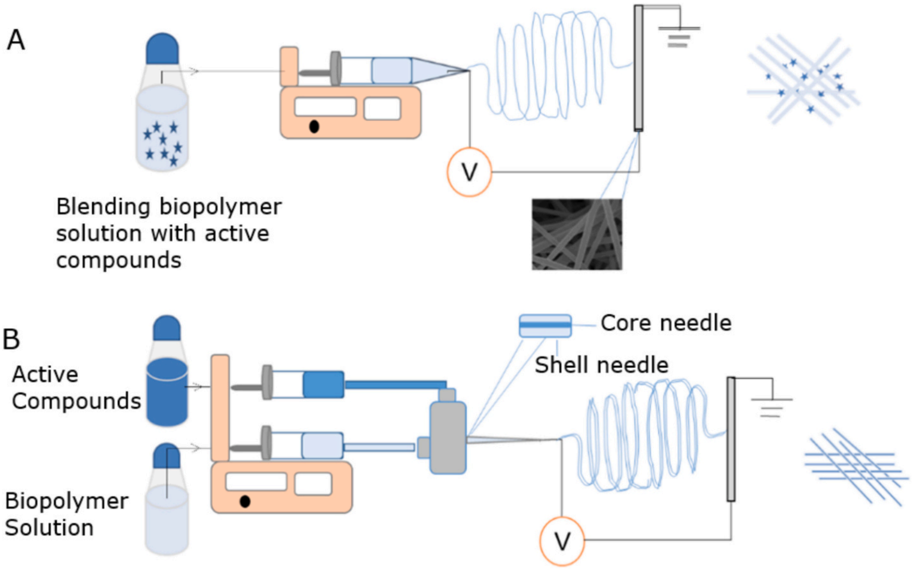

Fig. 14. (A) Uniaxial electrospinning, (B) Coaxial electrospinning [156].

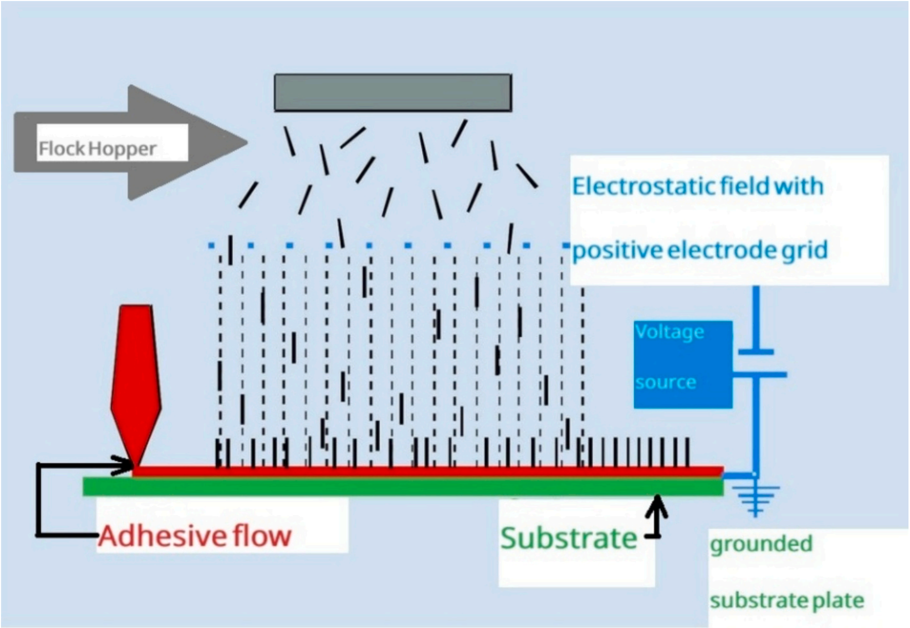

Fig. 15. The principle of electrostatic flocking.

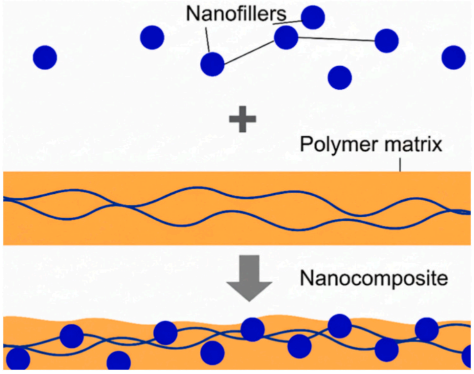

Fig. 16. Process illustration of Nanocomposite.

However, the applicability of soft lithography is generally limited to soft or flexible materials. It is not well-suited for rigid substrates such as the steel hulls of ships or ceramic components, thereby restricting its use in certain marine applications [43].

5.3. Etching

Etching is a widely used top-down fabrication approach for creating micro- and nanostructured surfaces by selectively removing material from a substrate. It enables precise control over surface roughness and patterning, making it suitable for antifouling applications. Etching techniques are generally classified into two categories: (a) dry etching, which includes methods such as lithography and plasma etching, and (b) wet etching, which involves the use of chemical solutions to dissolve specific regions of the material.

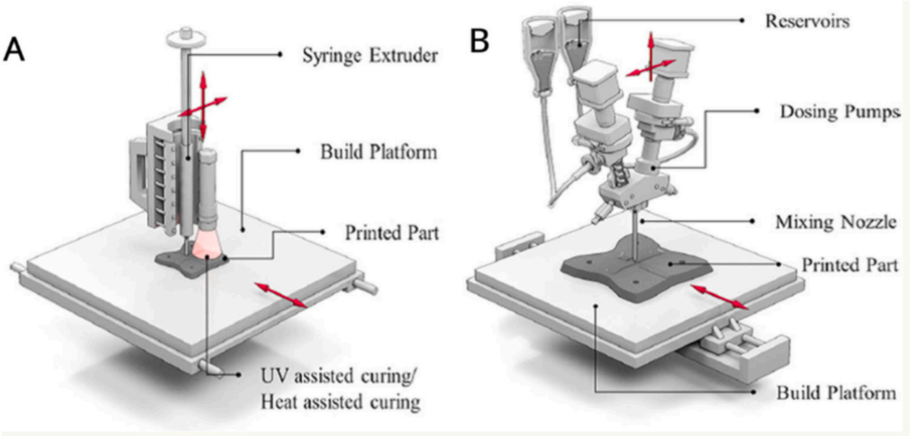

Fig. 17. Illustrative diagram showing AM technique [216].

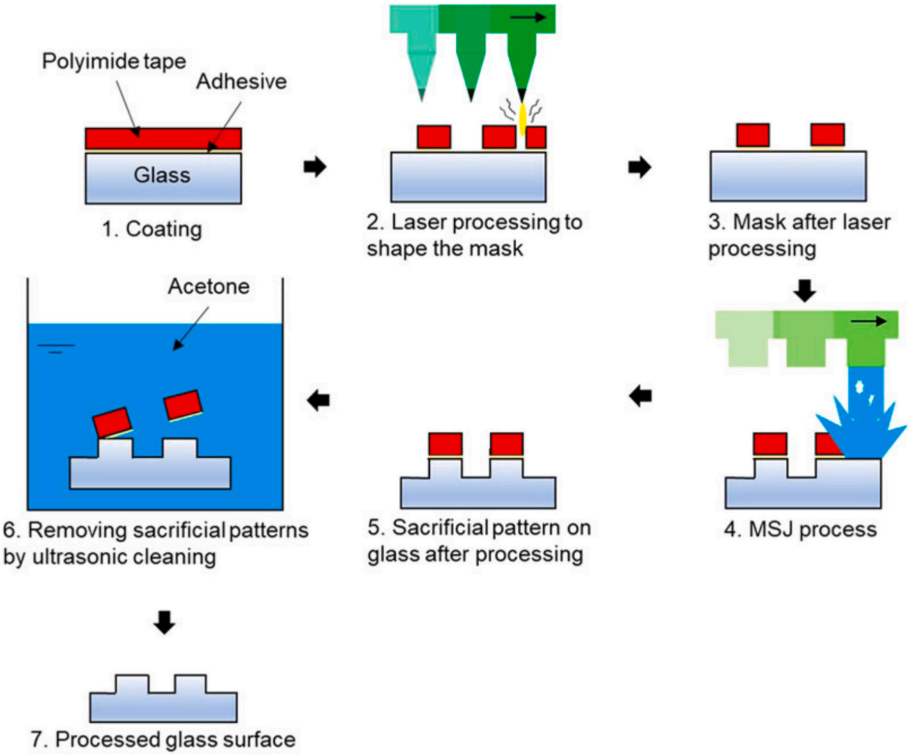

Fig. 18. Illustrative flowchart of MSJ micromachining [221].

5.3.1. Dry etching

This technique for fabricating micro and nanostructures as antifouling coatings, offers high resolution, precise pattern transfer, and compatibility with a variety of hard substrates. This method uses plasma or reactive gases to etch away material in well-defined patterns, enabling the creation of complex, high-aspect-ratio, and even sub-10 nm features that can effectively deter biofouling by physically preventing organism attachment or by mimicking natural antifouling surfaces [144]. Plasma Etching is convenient, clean and easy process with low environmental apprehensions.

Here high energy gas molecules like O_2 or CF_4 are bombarded on the substrate surface to create or modify surface features at the micro and nanoscale level, enhancing properties like hydrophilicity or hydrophobicity. O_2 plasma etching increases the surface oxygen content and hydrophilicity of carbon nanotube and nanodiamond electrodes, considerably improving their resistance to biofouling and boosting sensitivity for biosensing applications [145]. The substrate surface can be a metal, alloy or a polymer. Desired bioinspired surface can be created by repeating this process, resembling Lotus leaf of moth wing nanostructure [88]. Plasma etching can also expose embedded nanoparticles (TiO_2 in polymer membranes), enhancing photocatalytic and antifouling abilities. Drawback is that plasma etching may alter only the near-surface regions, so the durability of the antifouling effect depends on the stability of the modified layer under actual conditions [146].

This technique can be combined with Laser structuring methods like Pulsed Laser deposition, Laser direct writing, Laser textured templating or Laser interference Lithography to amplify pattern depth and achieve ultra-smooth, durable structures on both planar and non-planar surfaces [144]. These methods can be employed to fabricate bioinspired surfaces for metals, semiconductors, polymers and composites. It is highly cost effective giving excellent desired quality of the substrate plating [43]. The drawback remains the proper definition of laser parameters under

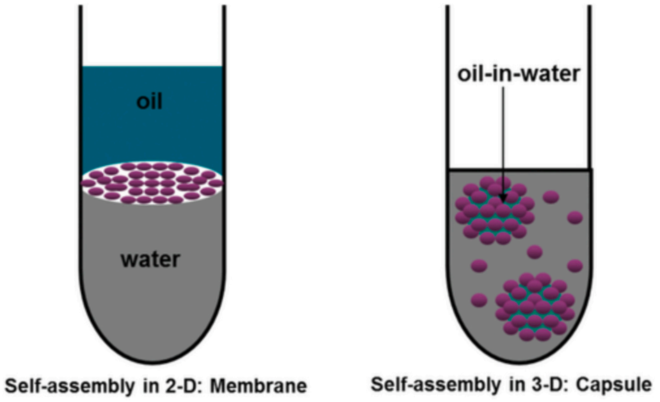

Fig. 19. Self-assembly of colloidal particles in 2D and 3D [236].

varying manufacturing conditions and the equipment cost. Moreover, Dry etching may cause damage or undesirable modification to sensitive substrates, and the use of reactive gases raises safety and environmental concerns [147].

Improvements in this process to address these drawbacks include Atomic Layer Etching (ALE), which achieves sub-nanometer precision through sequential ligand inhibition and fluorination cycles [148], and Cryogenic Etching at -100 °C, which suppresses chemical residues and reduces surface defects by approximately 70 % [149]. Fig. 12 is a schematic drawing explaining the plasma etching process.

5.3.2. *Wet etching or chemical etching*

It is an effective and simple technique for creating marine antifouling surfaces, especially on metal substrates like aluminium and magnesium alloys [150], [151]. In this method the substrate surface is chemically etched to develop a porous/roughened surface, which is then further modified by treating it with hydrophobic agents such as stearic acid or polydimethylsiloxane (PDMS). Fig. 13 is a schematic illustration of the process for creating microtextured surfaces for antifouling applications. A substrate such as titanium or stainless steel (shown in a neutral colour) is the base material which is to be microtextured. A mask layer (shown in yellow) is applied to the substrate.

This mask has a specific pattern that will determine the final microtexture. The areas covered by the mask will not be etched. An etching solution (shown in light blue) is applied to the substrate which chemically reacts and selectively removes the material not protected by the mask thereby creating the desired microtexture. After the etching process, the substrate is rinsed to remove any remaining etching solution. The texture so formed depends upon the parameters such as etching time, temperature, and solution concentration.

These hydrophobic surfaces can be further infused with lubricants, such as silicone oil, to form SLIPS. The resultant SLIPS coatings exhibit notable hydrophobicity, low sliding angles, and form a smooth, homogeneous oil layer that resists the adhesion of marine organisms [44]. Observations suggest that these chemically etched and lubricant-infused surfaces provide significantly enhanced antibiofouling and anticorrosion performance compared to an untreated or simply hydrophobic surfaces. Moreover, these coatings demonstrate good durability, maintaining their properties even after prolonged exposure to harsh marine

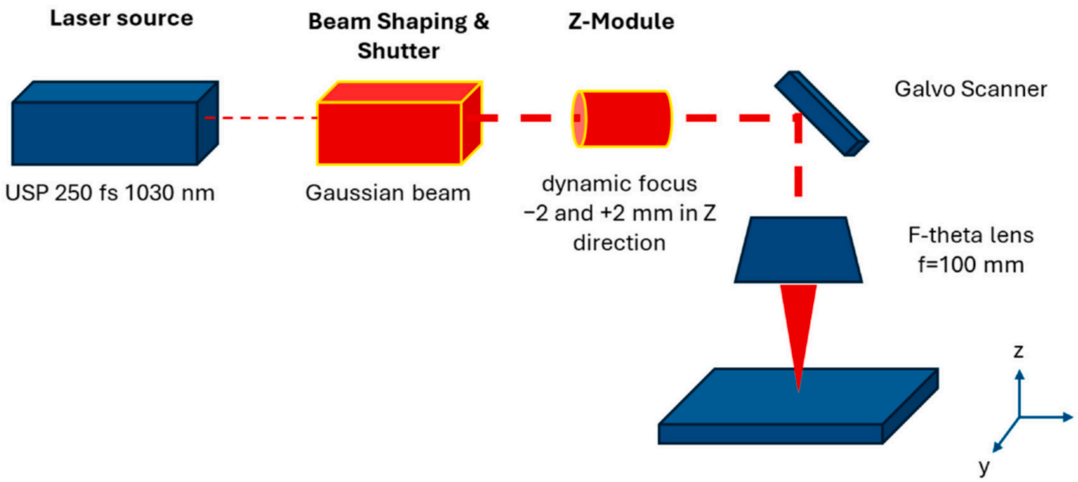

Fig. 20. Schematic diagram of picosecond laser surface texturing [251].

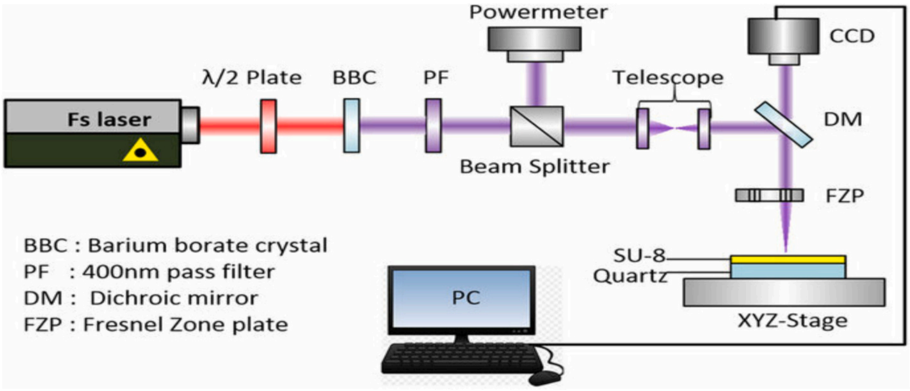

Fig. 21. Schematic setup of Femtosecond Laser for producing nanostructures [253].

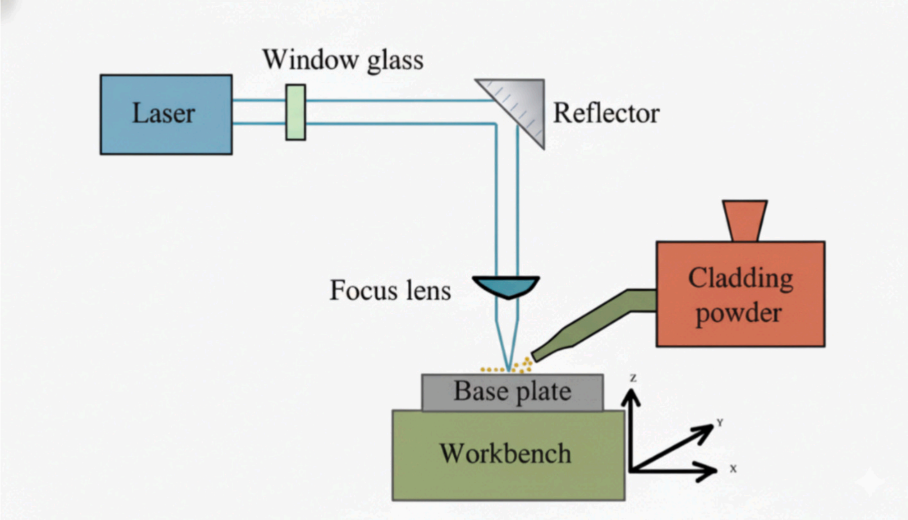

Fig. 22. Schematic setup of Laser cladding Technique.

conditions, such as immersion in lab generated acid rain or saline solutions.

The simplicity and efficiency of Wet etching make it a promising technique for large scale production of antifouling coatings on a variety of metal substrates for marine applications [151]. However, chemical etching, utilized for developing marine antifouling surfaces, has a few notable disadvantages. The method involves the use of hazardous substances, which raises concerns regarding environmental safety, particularly in marine environments where chemical byproducts can adversely affect aquatic organisms and ecosystems [152]. Achieving a uniform and precise etching over a large area or intricate surfaces is difficult, potentially leading to varying surface characteristics and diminished antifouling performance [153]. Additionally, chemical etching can weaken the mechanical integrity of the substrate, which may result in poorer adhesion of subsequent coatings and decreased durability in challenging marine conditions [56]. Furthermore, over-etching or uncontrolled etching of surfaces may produce irregular microstructure, which could inadvertently encourage fouling rather than prevent it if not carefully managed [154]. The process can also be expensive and challenging to implement on a large scale for substantial marine structures, often necessitating further surface treatments to ensure optimal antifouling efficiency [153].

To mitigate these problems, bio-inspired etchants, such as buffered citric acid, can replace hydrofluoric acid for more eco-friendly silicon nanowire fabrication [155]. Also, electrochemical templating, combined with anodic alumina membranes, can also create ordered nanopores with 90° sidewall angles. In summary, although chemical etching can alter surfaces to help prevent biofouling, its environmental implications, challenges in control, and potential to compromise coating durability restrict its practical usage as present marine antifouling coatings [154].

5.4. Electrostatic deposition

Electrostatic deposition encompasses techniques that utilize electric fields to assemble or deposit materials onto target surfaces in a controlled manner. These methods are particularly effective for creating hierarchical and porous surface structures suitable for antifouling applications. Two prominent approaches within this category are: (a) electrospinning, which generates nanofibrous mats with high surface area, and (b) electrostatic flocking, which orients short fibers vertically to create textured surfaces that resist fouling.

5.4.1. Electrospinning

Electrospinning is a technique where electric field is used to draw nanofibers from a polymer solution, for creating marine antifouling surfaces. Here ultrafine fibers with controlled morphology are deposited on a grounded collector, leading to a rough, porous surface that can effectively prevent fouling. By modifying the electrospinning parameters and polymer solutions, the surface properties can be tailored to fulfil a particular criterion and maximize antifouling performance. The polymer solution (melt) is forced through a fine capillary needle (spinneret) under high voltage. The electric field generates a Taylor cone at the tip of the needle, from which a jet of charged polymer solution is ejected. The jet is stretched and thinned down as it moves toward a grounded collector plate, forming nanofibers. These nanofibers are then deposited on the collector, creating a mat-like structure. Fig. 14 is a schematic drawing explaining uniaxial(14 A) and coaxial(14B) electrospinning.

In the uniaxial output (Fig. 14A), a simple spinneret is used to eject the solution through the electric field. Coaxial electrospinning (Fig. 14B) was developed by modifying the classical axial setup by arranging multiple solution feed systems to concurrently electrospin two or more polymer solutions from coaxial spinnerets. By carefully selecting the polymer and modifying the techniques, electrospun membranes can be made Superhydrophobic or Omniphobic (repelling both water and oils), further inhibiting fouling. The nanofiber network acts as a barrier, preventing the attachment of fouling organisms and particles on its surface. The challenge in production of electrospun fibers is optimization of electrospinning conditions, such as component concentration, voltage, distance between needle tip and collector, flow rate, temperature and humidity. Wrongly matched conditions and/or precursors can lead to failure in fiber formation and appearance of beads in the fibers, which decrease the mechanical stability of the materials produced.

Electrospinning offers several advantages in terms of controllability, particularly with respect to parameters such as applied voltage, tip-to-collector distance, solution flow rate, and substrate properties. These variables can be precisely adjusted to optimize fiber morphology and coating characteristics. However, controlling environmental factors like temperature and humidity poses significant challenges, especially in industrial settings such as shipyards or drydocks where electrospinning has to be implemented.

One of the primary limitations of electrospun antifouling surfaces lies in their mechanical weakness and durability. Electrospun nanofiber mats are inherently fragile and susceptible to damage from harsh marine conditions, including strong water currents, wave impact, sand abrasion, and physical friction from dock structures. This mechanical fragility restricts their long-term functionality. Furthermore, achieving strong adhesion between the electrospun fibers and underlying substrates such as ship hulls or offshore platforms is often problematic. Inadequate bonding can result in delamination or peeling, thereby diminishing antifouling performance [157]. Another concern is vulnerability to ultraviolet (UV) radiation, as many polymers used in electrospinning degrade upon prolonged sun exposure.

This degradation reduces molecular weight and tensile strength, thereby compromising antifouling functionality. For instance, studies have shown that just one hour of UV exposure can cause a 46 % reduction in the molecular weight of PLGA and a 35 % reduction in P (LLA-CL) nanofibers, along with a notable decrease in tensile strength. To mitigate this, researchers have incorporated UV-absorbing materials such as zinc oxide nanoparticles or strontium barium titanate nanorods into the polymer matrix.

While these additives significantly enhance UV resistance and material longevity, their effectiveness is closely dependent on proper concentration and homogeneous distribution throughout the fibers [158], [159] [160]. In terms of scalability, electrospinning is typically a batch process, which restricts continuous production and limits its industrial applicability. Conventional electrospinning exhibits a relatively low fiber deposition rate, making it difficult to meet the throughput requirements of large-scale marine coatings. Additionally, achieving consistent fiber diameter, morphology, and uniform thickness over extended surface areas requires precise control over multiple interdependent parameters such as voltage, solution properties, flow rate, and environmental conditions. This complexity adds further difficulty in adapting the process for high-volume, continuous production systems [161].

Material selection also presents notable constraints. The range of polymers suitable for electrospinning is limited, which restricts the inclusion of diverse antifouling agents. The polymers must possess suitable molecular weight to ensure adequate chain entanglement, and the solvent system must provide balanced viscosity and surface tension to support continuous fiber formation without beading. These requirements significantly narrow the options for integrating novel antifouling materials [162], [163]. Furthermore, incorporating inorganic nanoparticles or other non-polymeric antifoulants uniformly within the electrospun fibers is challenging, often leading to poor dispersion and uncontrolled release profiles [65]. The use of volatile organic solvents in electrospinning raises both environmental and occupational health concerns. Many of these solvents are toxic and contribute to air pollution, creating hazards for workers and the surrounding ecosystem. This concern becomes more pressing when water-insoluble polymers are used, as they necessitate strong organic solvents for processing [164], [165] [166].

To address these issues, researchers are exploring greener alternatives such as biologically benign solvents like acetic acid or acetone. These solvents offer lower toxicity and reduce environmental impact while maintaining effective fiber formation [167], [168]. Additional innovations include the use of deep eutectic solvents, ionic liquids, and techniques such as water-based or melt electrospinning, all of which aim to reduce or eliminate hazardous emissions [169], [170]. These sustainable approaches not only decrease environmental footprint but can also improve fiber properties and biocompatibility, thereby supporting eco-friendly manufacturing.

However, challenges remain in adapting these green methods across a wide range of polymers and ensuring they can be scaled for industrial-level production [170] [171]. In real marine environments, maintaining long-term performance remains a key challenge. In cases where antifouling functionality depends on the release of active agents such as biocides or zwitterionic molecules, sustaining a consistent release rate in dynamic aquatic conditions can be difficult. Rapid leaching may result in short-lived effectiveness and potential ecological harm. For example, electrospun fibers loaded with anti-quorum sensing agents initially inhibited biofilm formation as the hydrophilic component dissolved but eventually lost effectiveness due to depletion of the active compounds [172]. To overcome these limitations, the use of advanced electrospinning systems housed in environmentally controlled chambers has been proposed. These systems allow precise regulation of temperature, humidity, and other critical factors, thereby improving process reliability and product consistency in industrial applications [63], [173]. Another proposed innovation is Automated Collector Arrays, deploying robotic collectors for synchronized large-area deposition, increasing throughput 10 times [174].

5.4.2. *Electrostatic flocking*

Electrostatic flocking is a recent technique for creating marine antifouling surfaces by depositing vertically aligned fibers onto a substrate using an electrostatic field, often followed by additional surface modifications. Fig. 15 is a schematic diagram explaining the process.

The adhesive coated substrate passes through a high voltage electrostatic field. An electrode is used to charge the flocked fibers. The charged fibers become aligned with the electrostatic field lines of force and are attracted to the grounded electrode. The flock moves toward the adhesive coated substrate and becomes embedded. This method enables the fabrication of surfaces with unique micro- and nanotextured surfaces that physically deter the attachment of marine organisms. For example, slippery liquid-infused electrostatic flocking surfaces (S-EFSs) combine flocked fibers with a lubricant layer, resulting in complete resistance to mussel adhesion and significant reductions in the settlement of other fouling organisms such as tubeworms, tunicates, and barnacles as observed during long-term field tests [175]. Zwitterionic-modified flocked surfaces further boost antifouling property by creating hydrophilic, protein-resistant coatings that prevent both diatom and mussel attachment, with over 96 % stability after being exposed to artificial seawater for 30 days [176].

Bioinspired designs, such as mucus-like hydrogel films combined with hierarchical ciliary structures, also show strong resistance to microalgae and bacteria, biomimicking natural antifouling strategies [177]. Additionally, flocked surfaces have been shown to reduce the settlement of certain algae and encrusting animals in real-world marine environments [178]. The development and scalability of electrostatic flocking, along with its ability to support environmentally friendly, biocide-free coatings, make it a potential approach for practical marine antifouling applications.

However, the long-term durability of flocked surfaces may be challenged by mechanical wear due to severe abrasive forces in real world marine environments leading to detachment of fibers. The antifouling performance of these surfaces often depends on the stability of additional surface modifications, such as lubricant infusion or zwitterionic coatings, which may degrade or leach out after prolonged immersion, potentially diminishing their resistance to fouling. Improvements in this sector include pre-treating nylon fibers with O_2 plasma to enhance electrostatic adhesion by 50 % [174], and hybridizing epoxy-polyurethane adhesives to achieve submerged durability of over two years [179]. Finally, while flocked surfaces are generally considered environmentally friendly, the long-term environmental impact of synthetic fibers and any chemical additives used in the process is yet to be studied [175], [176].

5.5. *Nanocomposites*

Nanocomposites have emerged as a powerful player in the field of marine antifouling coatings, offering a combination of mechanical robustness, superhydrophobicity, and environmentally friendly properties. By integrating nanofillers such as zinc oxide, titanium dioxide, silicon carbide, graphene and cellulose nanocrystals into polymer matrices like polyurethane, silicone or chitosan, nanocomposite coatings exhibit enhanced surface roughness, reduced surface energy, resulting in self-cleaning and durable coatings that can significantly reduce biofouling in an actual marine environment [66], [154], [180].

An illustration of the process is shown in Fig. 16.

As for example, chitosan-zinc oxide nanocomposites and cellulose nanocrystal-based coatings have demonstrated good antibacterial and anti-diatom activity, as well as significant reductions in fouling under test conditions [181], [182]. Hierarchical nanocomposite coatings filled with disulfide nanorods or graphene provide long-lasting fouling release, superhydrophobicity, and mechanical durability without relying on conventional toxic marine coatings [183], [184]. Additionally, hybrid coatings combining silicone elastomers with nanocomposite hydrogels or amphiphilic copolymers have shown excellent antifouling performance and stability over extended periods in marine environment [185], [186].

Overall, nanocomposite-based antifouling coatings represent a promising, sustainable alternative to traditional toxic paints, with the potential for broader application in maritime industries [187], [188]. Drawbacks of nanocomposite coatings such as those based on PDMS, are prone to mechanical damage, weak adhesion to substrates, and limited static antifouling performance (while the ship is stagnant), which can restrict their long-term use in severe marine environments [183], [187]. In some cases, nanoparticles may become embedded within the resin matrix, reducing their surface activity affecting its antifouling functions [189]. There are also apprehensions about the potential environmental impact of nanomaterials, particularly if nanoparticles leach into the marine ecosystem over time [181]. Moreover, while many nanocomposite coatings show strong laboratory performance, their durability and antifouling efficacy can decrease during prolonged real-world exposure, especially under conditions of abrasion, UV radiation, and biofilm accumulation [183], [187], [189]. Lastly, scaling up production of these advanced coatings for large marine structures remains a technical and economic challenge [154], [187]. Proposed improvements involve using reduced graphene oxide as a dispersant framework to stabilize ZnO nanoparticles [190] and developing stimuli-responsive matrices, such as thermo-responsive hydrogels that release biocides only above 25 °C [191].

5.5.1. *Long-term environmental impacts of nanocomposite and advanced material-based antifouling coatings*

5.5.1.1. Reduced biocide leaching and ecological toxicity. Traditional antifouling coatings (e.g. tributyltin (TBT) and copper-based systems) released toxic biocides that cause severe ecological harm, including bioaccumulation in non-target species (e.g., oyster deformities) [125] and trophic transfer through aquatic food chain [192]. Nanocomposite coatings, such as TiO_2-SiO_2-reduced graphene oxide (TS-RGO), drastically reduce biocide leaching. TS-RGO coatings leverage photocatalytic properties to generate reactive oxygen species (ROS), inhibiting biofilm formation without releasing heavy metals. Lab tests show >90 % inhibition of Pseudomonas biofilm adhesion over 12 months [193]. Similarly, graphene oxide-polydimethylsiloxane (PDMS) nanocomposites minimize biocide usage by augmenting hydrophobic fouling-release properties [193].

5.5.1.2. Nanoparticle persistence and bioaccumulation risks. Persistence refers to the duration for which nanoparticles remain in a specific environment. Although engineered nanomaterials such as cerium oxide (CeO_2) nanoparticles exhibit relatively low toxicity, they display considerable long term environmental persistence. Within aquatic food chains involving algae, zooplankton, and fish, CeO_2 nanoparticles accumulate in organisms but show minimal biomagnification, with a biomagnification factor of less than one [194]. However, trophic transfer efficiency ranges from 10 to 20 % [192], which may pose potential risks to benthic ecosystems. These ecosystems consist of organisms inhabiting the bottom regions of aquatic environments such as oceans, lakes, and rivers, where sediments act as sinks for nanoparticles [195]. Silver nanoparticles also bioaccumulate in marine copepods such as *Tigriopus japonicus* through waterborne exposure, exhibiting bioaccumulation factors ranging from 1200 to 1800 [196].

5.5.1.3. Degradation and transformation in marine environments. Advanced materials are being designed to achieve controlled degradation in order to reduce environmental persistence. Cellulose nanocrystal (CNC) based coatings are fully biodegradable and can degrade within six to twelve months in seawater without leaving any microplastic residues [197]. Butenolide antifoulants undergo rapid degradation under ultraviolet light, with a half-life of 3.9 days at 40 °C, but can persist for more than sixty-four days in cold waters at 4 °C [198]. MXene reinforced hydrogels exhibit self-healing properties that minimize material loss, while their photothermal degradation behaviour further reduces long term accumulation in marine environments [199].

5.5.1.4. Non-toxicity mechanisms vs. unintended effects. Nature inspired strategies, such as microtextured surfaces that mimic shark skin, physically prevent organism adhesion and completely eliminate the need for biocides [125] [123]. However, superhydrophobic nanocomposites like cellulose nanocrystal polyvinyl alcohol systems may inadvertently trap organic matter, leading to changes in local microbial communities [197] [200]. Zinc oxide nanoparticles incorporated into chitosan composites exhibit no organ specific toxicity in zebrafish (*Danio rerio*) embryos, yet the dissolution of these particles releases zinc ions (Zn^{2+}) that can disrupt algal photosynthesis at concentrations exceeding 1 mg/L [201].

Despite these advances, field studies have highlighted several challenges related to the long-term performance of such coatings. Eco friendly copper alternatives demonstrate approximately 50 % less fouling than traditional coatings in wave exposed environments but require reapplication every two to three years [202]. Similarly, polydimethylsiloxane nanocomposites can sustain fouling release properties for more than five years but tend to accumulate diatoms in stagnant waters [203] [204].

5.5.2. *Analysis of critical trends and environmental trade-offs*

5.5.2.1. Positive Long-term outcomes. Non biocidal coatings help reduce trophic damage by lowering the risk of bioaccumulation in aquatic ecosystems. For instance, fullerenol nanoparticles exhibit negligible trophic transfer within aquatic food webs [205]. Hydrogels and cellulose based materials contribute to carbon neutral degradation as they mineralize into carbon dioxide and water during breakdown [206]. However, some concerns regarding nanoparticle persistence remain. Carbon nanotubes inhibit cyanobacterial growth by 40 to 60 % in biofilms, thereby affecting primary productivity [207] [208]. In addition, about 30 to 50 % of released silver nanoparticles settle in sediments, where sulfidation processes prolong their environmental persistence [209] [210].

5.5.3. *Future mitigation strategies*

Future mitigation strategies focus on developing more sustainable and efficient antifouling materials. Dragonfly wing inspired surface textures have shown the potential to reduce diatom adhesion by about 70 %, offering a biomimetic approach to minimize fouling [154]. Self-healing composites such as poly (urea thiourea)/tannic acid coatings can repair surface damage, thereby extending service life and reducing the need for frequent replacement [210]. However, significant regulatory gaps remain, as standardized OECD and ISO test methods for evaluating nanoparticle ecotoxicity are still underdeveloped, which hinders comprehensive environmental risk assessment [211].

5.5.4. *Conclusion: Balancing innovation and sustainability*

Nanocomposite coatings represent a major advancement toward ecofriendly antifouling technologies, achieving a reduction of 60 to 80 % in acute toxicity compared to coatings from the tributyltin era [212]

[213]. However, the persistence of nanoparticles in benthic zones and their unintended trophic effects highlight the need for comprehensive lifecycle assessments. Future research should focus on quantifying the degradation kinetics of engineered nanomaterials by determining their half lives in marine sediments [214].

Long term field surveillance, extending over ten years or more, is required to evaluate their ecological effects on coral reefs and seagrass ecosystems. The development of circular design approaches, such as upcycled nanocomposites with inherent recyclability, can further enhance sustainability [123] [199]. Ultimately, the transition to green antifouling technologies depends on balancing material innovation with rigorous ecotoxicological validation [215] [125].

5.6. Additive manufacturing (AM) or 3D printing

This rapidly developing technology is now being used to manufacture 3D models designed by computers, using layer by layer (LBL) technique. The schematic diagram below illustrates the 3D printing process. Fig. 17A explains 3D printing with a single feedstock. To create a model through direct writing, a computer CAD model utilizing various derivatives is necessary. This method employs a viscous ink as a feedstock, which may consist of materials such as ceramic particles, metal particles, hydrogel, polyelectrolytes, polymeric substances, or extracellular matrices. The liquid feedstock material or slurry hydrogel is kept in a container connected to the syringe.

A computer-controlled syringe exerts the necessary mechanical or pneumatic pressure to extrude the feedstock solution. The extruded solution is then deposited onto the building platform in a layer-by-layer manner. Various mechanisms, including UV polymerization and post-fabrication heating cause the ink to solidify. Fig. 17B explains Multiple material 3D printing with micro-fluidic print heads, that can swiftly switch between different inks while using the same single nozzle print heads, benefiting from tool path planning and the programmable assembly of functional materials.

The method is simple, reliable and offer precise control over surface architecture with the ability to create complex, biomimetic micro- and nanostructures that deter biofouling and can be customized through computer designing. Materials like metals, alloys, ceramics, composites, nanocomposites, hydrogels, and amphiphilic polymers and concrete has been used for AM [154], [217].

However, while AM seems to be a potent player, its application in large-scale marine environments is still in early stages, and further research is needed to address challenges such as scalability, long-term durability, and cost-effectiveness [154], [218]. Also, soft materials which are more appropriate for bioinspired antifouling coatings cannot be used much in AM and is still in the developing phases.

One proposal to address the limitations of this technique is multi-material printing to co-print silicone and fluorinated acrylates for dual topographical and chemical functionality [219], and by using vapor smoothing to post-process Fused deposition modelling (FDM) prints with acetone vapor, reducing surface roughness to $Ra < 50$ nm [220].

5.7. Micromachining

Micromachining enables the creation of bioinspired marine antifouling surfaces by replicating natural micro- and nanostructures. When combined with chemical or biological modifications, these surfaces offer highly effective, durable, and environmentally friendly antifouling solutions for marine applications. Methods such as laser surface texturing, reactive ion etching, and molding are used to replicate these natural patterns onto engineering materials (e.g., stainless steel, aluminium, PDMS). Micromachining technique can be broadly subdivided into 4 groups; Mechanical, Electrothermal, Electrochemical and Abrasion-ablation, and is discussed in greater details in section 6. Mechanical micromachining uses super hard tools like monocrystalline diamonds to create a wide range of patterns on the substrate plate.

The size of the pattern depends on the size of the cutting tool. Fig. 18 illustrates a type of mechanical machining called Micro-slurry Jet machining (MSJ). Here, Micro-convex structures were developed on a soda lime glass using this technique. Masking on the glass was done with a polyamide tape with silicon adhesive. The topography was created on the polyamide tape with a CO_2 Laser machine. Then MSJ process was performed and finally the masking was removed by ultrasonic cleaning to expose the desired convex microstructure on the glass plate.

Electrothermal Micromachining (Electric Discharge, Laser) employs thermal energy generated by electrical discharges (EDM) or focused laser beams to remove material. Electrochemical Micromachining (Milling, Drilling, Plating) utilizes controlled electrochemical reactions to dissolve material at the micro-scale, often without inducing thermal or mechanical stress. Abrasion and Ablation involve mechanical wear using abrasive particles or tools to remove material, such as abrasive-jet machining and abrasive flow finishing.

Efforts are being made to improve precision by introducing error compensation methods. Optimization of micro-milling, turning and grinding process delivers designed patterns. Although being a cost-effective method, drawback is that the resolution of the surface fabricated by this method is limited. Other drawbacks are thermal distortion during laser ablation and the high cost incurred for large-area patterning [43] [222], [223], [224], [225], [226], [227], [228], [229], [230], [231], [232].

Innovations like hybrid laser-chemical etching, which combines ultrashort pulses with a $NaHCO_3$ etchant for crack-free microchannels [233], and the use of bio-mimetic algorithms to optimize Sharklet patterns via ML-driven fluid dynamics simulations [102], offer pathways for improvement. Though not a marine AF product, Sharklet Technologies, Inc. have developed commercially available adhesive films and surfaces specifically for areas which are frequently touched or are prone to bacterial infection (e.g. door handles, point-of-sale counter tabletops, washrooms). The produced surfaces mimic the microtopography of a sharkskin using advanced micro/nano manufacturing methods such as photolithography, nanoimprinting, and high-precision mold manufacturing techniques, thus repelling colonization of germs and bacteria. Micrograds (20-50 μm depth) produced by laser-engraving on PTFE-coated silicon exhibit ultralow oil adhesion ($<5\mu N$) preventing macrofouling attachment. This product has been commercialized as anti-fouling panels for tidal energy turbines [234] [235].

5.8. Self-assembly

All living organisms grow and reproduce by this method, from a single cell to multi-cellular creatures, and finally form a predetermined or predefined structure, like a human being or a banyan tree. This self-assembly starts from the atomic to microscopic stage, and the shape, scale and nature of the pattern depends on the unit building blocks. This natural technology may be utilized to manufacture bioinspired antifouling coatings. Available building blocks such as metals, nanoparticles, polymers, surfactants, and lipids can be utilized for self-assembly. As an example, Fig. 19 shows a schematic image showing Self-assembly of Colloidal nano-particles in 2D and 3D showing the formation of membrane and capsules at the liquid–liquid interface.

The resulting patterns act as templates that are transferred into or onto underlying layers by etching, stamping or deposition. For example, LBL-assembled coatings inspired by Laminaria japonica combine microstructural features and encapsulated natural antifoulants to achieve excellent resistance against bacteria and diatoms [237]. Self-assembled monolayers (SAMs) on gold and silica surfaces can be customized to be hydrophilic, hydrophobic, or amphiphilic, thus providing molecular-level control over surface infestation with biofoulants [238]. Hierarchical self-assembly of microgel spheres or ciliary structures can impart self-healing, superoleophobic, and self-cleaning properties, further enhancing antifouling performance and durability [177], [239]. Additionally, self-generating and self-renewing zwitterionic polymer surfaces leverage hydrolysis or enzymatic degradation to continuously refresh the antifouling layer, maintaining long-term effectiveness in marine environments [91]. To achieve the desired patterns, the properties such as polarity, surface properties, magnetic dipole, shape, charge and mass of building blocks are taken into consideration. These properties determine the interactions between building blocks. Hence, the design and selection of the building block is important to obtain well-defined patterns and functions. To manufacture surfaces using this technique the important criteria are (i) the blocks should be interchangeable (ii) blocks should interact with each other, (iii) Suitable environment to be present like the liquid phase, with smooth surface and boundaries, and (iv) self-assembly should be reversible or adjustable.

This method has been used to fabricate bioinspired surfaces of butterfly wings, lotus leaves and rice leaves [240]. Noteworthy limitations of this process include the difficulty in achieving accurately and uniformly assembled structures on extensive or intricate hull surfaces, which may result in variable antifouling effectiveness and restrict the scalability for the maritime shipping industry. The resilience of self-assembled coatings in harsh marine environments, such as strong currents, varying temperatures, and mechanical/abrasive wear, can be tricky, as these conditions might compromise the delicate micro- or nanostructures vital for antifouling. Furthermore, the long-term strength and mechanical stability of self-assembled layers often fall short compared to traditional coatings, potentially necessitating more frequent upkeeping or reapplication. Certain self-assembly methods may also entail complicated chemistries or require precise environmental conditions, which can drive up production costs and hinder practical implementation at the shipyard/repair yard/drydock. Lastly, although self-assembly can minimize the reliance on harmful biocides, its antifouling effectiveness may still be inferior to that of conventional coatings, particularly against a wide range of marine organisms [44], [218].

These drawbacks may be addressed, and the characteristics of self-assembled surfaces can be enhanced through field-assisted assembly, where applying oscillating electric fields (10 kHz) accelerates Janus particle alignment by a factor of 100 [241]. Further improvement can be achieved by designing marine-adapted zwitterionic copolymers that exhibit salinity-triggered assembly [242]. Commercially available coatings based on self-assembly techniques include NuSil Technology's silicone elastomers, Econea®-embedded coatings, and Nippon Paint's A-LF-Sea. Products such as NuSil Technology's silicone elastomers utilize self-assembled polysilsesquioxane (PSQ) networks containing quaternary ammonium chains, which create hydrophobic surfaces that reduce bioadhesion strength by 70-90 %, allowing fouling to be removed by water shear forces during vessel movement.

These coatings are applied to cargo ships and offshore oil platforms, extending dry-dock intervals by 2- 3 years [243]. Econea®-embedded coatings (e.g., Hempel's Globic Series) employ self-assembled acrylic copolymers with microphase-separated hydrophilic and hydrophobic domains. This architecture disrupts biofilm adhesion and reduces bacterial attachment by more than 95 %. Such coatings are used in cruise ships and aquaculture nets in Europe and the Asia-Pacific region [244] [245]. Nippon Paint's A-LF-Sea incorporates self-assembled vinyltrimethoxysilane (VTMOS)-modified SiO_2 nanoparticles into PVDF matrices, forming micro- and nano-hierarchical structures with water contact angles greater than 160°, and are widely applied in high-speed ferries across Southeast Asia [246]. A summary of the eight techniques described in the preceding section is presented in Table 2.

6. Concept of micromachining for creating bioinspired marine antifouling surfaces

Marine organisms like crabs and seaweeds have evolved surface structures that naturally resist fouling. Surfaces of these living organisms often feature hierarchical micro and nano roughness, superhydrophobocity, and complex geometries that minimize attachment of fouling organisms.

Micromachining or ultra precision machining is an emerging and promising technology for manufacturing bioinspired marine antifouling surfaces. By mimicking the micro and nanostructures naturally adopted by marine organisms, micromachining enables the fabrication of surfaces that resist the attachment of marine fouling organisms. These engineered microtopographies, often combined with chemical modifications, offer a promising, non-toxic, and eco-friendly alternative to traditional antifouling coatings. Various micromachining technologies presently available in the industry are summarized in Table 3.

These techniques are valuable for fabricating micro- and nanostructured surfaces with tailored antifouling properties suitable for marine applications.

In particular, electrothermal micromachining methods such as laser-based surface modification enable precise control over surface topography. Lasers can be employed to replicate naturally occurring antifouling textures (biomimetic designs) or to engineer novel surface patterns that inhibit the adhesion of marine organisms. This approach provides a durable, non-toxic alternative to conventional antifouling paint systems [88], [230], [232], [247], [248]. The mechanisms and techniques are discussed in detail in the following section.

6.1. Ultrafast laser texturing

Femtosecond and picosecond lasers are employed to create precisely controlled micro- and nano-scale surface patterns on metallic substrates. These laser-induced textures can be customized to impart specific surface characteristics, such as superhydrophobicity or superhydrophilicity, both of which contribute significantly to antifouling performance by minimizing the adhesion of marine organisms [232], [248].

6.1.1. Laser surface texturing

Laser surface texturing has been used to create biomimetic of Shark skin on Al_2O_3/TiC ceramic plate [249] . This surface texturing creates micro-grooved patterns that mimic the riblet structures of shark skin. This approach significantly improves the tribological properties of the ceramic, as the textured grooves reduce friction by decreasing the contact area, trapping wear debris, and serving as lubricant reservoirs, thereby enabling more effective and sustained lubrication during sliding or cutting operations. The laser used for this surface texturing was Nd: YAG laser with the wavelength of 1064 nm, average power of 4 W, repetition rate of 20 kHz, scanning speed of 100 mm/s. This bionic shark skin textured surface created using Laser surface texturing was followed by electrohydrodynamic atomization of WS_2 (Tungsten disulfide) coating, and demonstrated a significant reduction in coefficient of friction, from 0.44 for a polished plate down to 0.3 for the textured surface (a reduction of 32 %).

Nanosecond laser has been used to mimic surface texture of purple orchid leaves on a 316 L Stainless steel surface. After acid wash to remove the surface oxides, nanoscale organomettalic compounds were electrodeposited on the laser patterned microstructure. The prepared surface topography demonstrated improved abrasion resistance and a Water Contact Angle (WCA) of 163.54 ± 1.59° [250]. Fig. 20 [251] explains and demonstrates the surface irradiation by a near infrared polarized Picosecond Laser on a silicon crystal.

The sample consists of a polished p-type single-crystal silicon substrate. An ultrafast laser system was utilized to produce a Gaussian spatially distributed linearly polarized light. The laser power is continuously and precisely adjusted using a combination of a half-wave plate and a polarizer. The objective lens focuses the laser beam, which is directed vertically onto the surface of the sample in air. A zero-order quartz half-wave plate is positioned in front of the objective lens to modify the direction of laser polarization. A three-dimensional motion platform allows for accurate movement of the sample within the laser's

Table 2
Summary of Fabrication Techniques for Marine Antifouling Coatings.

Coating Type/ Technique	Mechanism	Effectiveness & Advantages	Limitations	Environmental Impact	Durability
Layer-by-Layer (LBL) Deposition	Multilayered films by alternate deposition of oppositely charged polymers. Creates controlled hydrophilic/PRC or biocide-releasing surfaces.	Precise nanoscale control over thickness and composition. Can create complex, multi-functional layers.	Slow, water-intensive process. Not easily scalable to a ship's hull. Mechanical stability can be low without post-processing.	Generally low, as it often uses water as a solvent. Depends on the toxicity of the polymers used.	**Poor to Moderate:** The electrostatic bonds can be weak in harsh marine conditions unless chemically cross-linked.
Electrodeposition	Uses electric current to deposit a coating (polymer or metal) from a solution onto a conductive substrate. Can be used to create textured or biocide-infused coatings.	Provides a very uniform coating, even on complex shapes. Good control over thickness.	Requires a conductive surface. The composition of the bath can be complex and hazardous.	**Moderate to High:** Plating baths can contain heavy metals or toxic chemicals, requiring careful waste management.	**Good to Excellent:** Can create very hard, dense, and well-adhered coatings.
Chemical Vapor Deposition (CVD)	Gas-phase chemical precursors react with the substrate to form a solid, thin film. Used to create ultra-hard, low-surface-energy coatings (e.g., diamond-like carbon).	Creates extremely high-quality, pure, and uniform films. Can coat complex shapes.	High cost and energy consumption and requires a vacuum chamber. Impractical for large surfaces like a hull.	**High:** Often involves high temperatures and toxic, flammable, or corrosive precursor gases.	**Excellent:** Produces some of the most durable and abrasion-resistant coatings available.
Templating / Soft Lithography	A master pattern (template) is used to mold a liquid polymer (like silicone), creating a negative replica. The primary method for making bio-inspired microtextured surfaces.	Relatively low-cost and highly effective for creating micro-patterns over large areas. Very versatile.	Resolution is limited by the template. Risk of defects during mold release. The template itself can wear out.	**Low:** Usually involves benign polymers like silicone (PDMS). Minimal chemical waste.	**Moderate:** Durability is determined by the polymer used. The micro-patterns themselves can be fragile and prone to damage.
Dry Etching (Lithography & Plasma etching)	A pattern is defined using light (photolithography), and then a plasma (ionized gas) is used to precisely etch the pattern into the surface.	Extremely high precision and resolution for creating perfect micro- and nano-patterns.	Extremely slow, complex, and expensive multi-step process. Only feasible for ships' hull coating.	**High:** Uses hazardous chemicals (solvents, photoresists) and is a high-energy process.	**Excellent:** The pattern is etched into the bulk material, making it inherently durable (though features can still be damaged).
Wet Etching (Chemical Etching)	Uses liquid chemicals (highly acidic/basic) to selectively dissolve material and create a pattern, often guided by a protective mask.	Simpler and much cheaper than Dry etching.	Less precise than Dry etching, as chemicals can etch sideways (undercutting). Generates significant chemical waste.	**High:** Involves the use and disposal of large volumes of corrosive and often hazardous chemicals.	**Good:** The resulting pattern is part of the bulk material.
Electrospinning	High voltage electric field is used to draw a polymer solution into nanofibers, creating a highly porous, non-woven mat. Used to create superhydrophobic surfaces.	Creates a high surface area with a unique texture that can trap air to reduce friction and deter fouling. Can encapsulate biocides.	Slow production rate for large areas. Resulting mat has poor mechanical strength and abrasion resistance.	**Moderate:** Often relies on volatile organic compounds (VOCs) as solvents, which are released during the process.	**Poor:** The nanofiber mat is mechanically weak and easily damaged by physical contact or shear forces.
Electrostatic Flocking	An electrostatic field is used to apply short, charged fibers vertically onto an adhesive-coated surface, creating a dense, brush-like texture.	Creates a unique physical texture that is difficult for larger organisms to settle on.	The durability of the adhesive layer and the fibers themselves in a marine environment is a major concern.	**Low:** The process itself is low-impact. Depends on the adhesive and fiber materials chosen.	**Poor:** Highly susceptible to abrasion and shear forces, which could easily wipe off the fibers from the surface.
Nanocomposites	Nanoparticles (e.g., silica, graphene, copper oxide) are mixed into a standard coating matrix (e.g., silicone, epoxy) to enhance its properties.	Highly practical and versatile. Can improve mechanical strength, create nano-scale roughness, or provide controlled biocide release.	Difficult to achieve uniform dispersion of nanoparticles free of clustering. Long-term environmental impact of leached nanoparticles to be surveyed.	**Moderate:** Primary concern is the potential eco-toxicity of nanoparticles leaching into the ocean over time.	**Good to Excellent:** Often used specifically to *improve* the durability and abrasion resistance of the base coating.
Additive Manufacturing (AM) / 3D Printing	Builds a surface layer-by-layer directly from a digitall fed design. Used to prototype and create highly complex, bio-inspired hierarchical structures.	Unmatched design freedom to create complex geometries that are impossible with other methods. Ideal for rapid prototyping.	Extremely slow and expensive for large areas. Material selection is limited. Surface finish may require post-processing.	**Moderate:** Varies by method. Can involve plastic waste (FDM) or chemical resins and solvents (SLA).	**Moderate to Good:** Durability depends on the printing ink material and the strength of adhesion between layers.
Micromachining	Uses a physical tool, such as a high-precision cutter or a laser beam (laser ablation), to directly carve micro-patterns onto a surface.	Creates very precise and durable patterns. No risk of delamination as the pattern is part of the bulk material.	Extremely slow serial process, making it expensive and time-consuming for large-scale applications.	**Low to Moderate:** Low chemical waste, but can be a high-energy process, especially for lasers.	**Excellent:** The patterns are integral with the surface, making them very robust.
Self-Assembly	Molecular blocks (e.g., block copolymers) that spontaneously organize into a desired nanoscale structure (e.g., an amphiphilic surface) when applied.	A “bottom-up” approach that can create perfect, ordered nanostructures with minimal energy. Forms the basis for advanced PRC/FRC.	Complex and expensive to synthesize the required molecules. Controlling the assembly over large, imperfect surfaces is a major scientific challenge.	**Low:** Potentially very efficient and low-waste once the molecules are synthesized.	**Moderate to Good:** Durability depends on the stability of the assembled structures and their adhesion to the substrate.

Table 3
Summary of Micromachining techniques.

Process➔	Mechanical Micromachining	Electrothermal Micromachining	Electrochemical Micromachining	Abrasion/Ablation Technique
Type of Technique	Precision cutting, milling, or shaping at micro-scale using mechanical tools	Localized heating (e.g., laser, EDM) to remove or modify material at micro-scale	Material removal via controlled electrochemical reactions at micro-scale	Removal or modification of surface layers using high-energy sources (e.g., laser ablation, sandblasting)
Mechanism	Physical removal of material to create micro/nano-patterns that mimic natural antifouling textures	Thermal energy melts or vaporizes material, forming microstructures or altering surfaces	Electrolytic dissolution forms complex micro-patterns without mechanical or thermal damage	High-energy pulses (laser, etc.) ablate surface, creating micro/nano features or cleaning biofouling
Key Features / Applications	Produces durable, precise biomimetic textures; enhances antifouling by disrupting organism attachment; suitable for hard substrates	Enables rapid, non-contact patterning; can create superhydrophobic or hierarchical surfaces; useful for complex geometries	Achieves high aspect ratio, smooth microstructures; avoids heat/ mechanical damage; suitable for metals and alloys	Effective for cleaning and texturing; can induce superhydrophobicity; removes biofouling and creates antifouling surfaces
Citations	[228], [229]	[228], [229]	[222], [223], [224], [225]	[228], [229]

focal plane. The orientation of the crystal, the direction of laser polarization, the direction of sample scanning, and the relationship of the sample's scanning direction to the crystal's axis were established using electron backscatter diffraction (EBSD).

6.1.1.1. Femtosecond laser direct writing (FLDW) technology. This technique is being utilized to fabricate biomimetic 3D patterns on metallic and other surfaces. This technology offers several advantages in fabricating biomimetic patterns for antifouling coatings, including high precision, versatility, contactless processing, exceptional precision and structure quality across a wide range of materials, and mask-free processing, enabling the creation of intricate micro- and nanostructures with minimal thermal damage [252]. FLDW setup schematic drawing is shown in the Fig. 21 below [253].

In the Fig. 21, λ/2 plate was used to change polarization of the laser. The experimental set-up consisted of a Ti:Sapphire femtosecond laser, a beam delivery system, a high numerical aperture Fresnel's zone plates as focusing optics, CCD imaging system for monitoring nanostructure fabrication process, and a piezo-electric-stage and its control system. The sample is SU-8 (a negative, epoxy-based photoresist) coated on quartz. Nanowires and nanogrooves were created using this experimental setup.

FLDW is also suitable for operations where heat-induced changes are uninvited, like in biomedical applications (LASIK). FLDW can accurately control the laser-substrate plate interaction, allowing for the fabrication of highly complex patterns on a wide range of materials, including metals, ceramics, and polymers. It can directly write patterns and textures without the need for masks or other traditional lithography methods, thereby simplifying the fabrication process [252].

Cao et al. [252] used FLDW based on Two Photon Polymerization (TPP) to create cone and pinecone structures resembling the lotus leaf hydrophobicity. Lotus leaves are famous for their self-cleaning and superhydrophobic characteristics, which stem from their distinct micro/nano hierarchical surface structure. The leaf surface consists of papillae-microscale projections ranging in diameter from 2 to 8 μm and in height from 6 to 12 μm, which are further adorned with nanoscale wax crystalloids or branched formations. This dual-scale design is essential: the microscale papillae minimize the contact area with water droplets, while the nanoscale wax boosts water repellence and hinders water from seeping between the papillae, leading to high contact angles and low adhesion. The hierarchical structure not only provides superhydrophobic qualities but also allows the leaf to retain its characteristics under various environmental conditions, such as rain or submersion, by resisting water intrusion and promoting self-cleaning [254], [255].

The experimental TPP fabrication was conducted in a femtosecond laser processing system (FemtoLAB-MPP, Workshop of Photonics, Lithuania), which was equipped with a laser (514 nm wavelength), a high-resolution stage (Aerotech) and oil immersed objective lens (63×, 1.4 NA, Zeiss). The collimated beam diameter before the focusing lens was measured as 5 mm and the focused laser spot diameter was calculated as 280 nm. The optimum processing parameters (laser power 2.2 μW, hatch space and layer thickness 100 nm) can generate structures with dimensions close to the design values by precisely tuning the laser intensity and scanning speed.

There was no trace of printed structure when the laser power was below the threshold limit of 0.8 μW. The pinecone structures exhibited superior performance compared to the ones with no nano-scale structures, indicating that superior hydrophobicity can be achieved by designing the micro/nano hierarchical structures. By increasing the density of the nano cones in a micro/nano hierarchical structure hydrophobicity was found to improve. While FLDW technology can be used for precision and versatility in the fabrication of micro/nanostructures, its limitations include low throughput, material and depth constraints, difficulty in fabricating uniform and defect-free surfaces, and high equipment costs. Despite its precision and versatility, several factors currently limit the widespread adoption of Femtosecond Laser Direct Writing (FLDW) for large-scale manufacturing applications. One of the primary limitations is its low processing speed, as FLDW patterns surfaces in a point-by-point or line-by-line manner, resulting in slow fabrication rates that are unsuitable for large-area or high-throughput production. [256], [257], [258].

Additionally, while FLDW is compatible with a variety of materials, challenges arise when working with substrates like crystalline silicon, which exhibit poor energy absorption, thereby limiting the achievable modification depth and overall quality. In such cases, specialized techniques or alternative pulse regimes may be required to improve performance. Controlling the depth of modification, especially in thicker substrates, is another challenge, often affecting the uniformity and structural consistency of the fabricated features [256]. Moreover, the high cost of femtosecond laser systems and the precision motion stages necessary for FLDW significantly increases the overall fabrication expense [259]. The technical complexity of the process, which demands fine control over laser parameters and environmental conditions, further necessitates skilled personnel and advanced instrumentation, adding to the operational burden [256], [259].

6.1.1.2. 2.5-dimensional femtosecond laser surface microstructuring. A recent development to address the low processing speed, limited scalability and precision of FLDW is the proposed 2.5Dimensional (2.5D) Femtosecond Laser surface microstructuring. Jaka Petelin et al. [258] experimentally demonstrated a new concept of a 2.5D surface structuring that boosts processing throughput and precision simultaneously, when compared to traditional laser surface structuring techniques like FLDW. Unlike traditional FLDW, which typically produces either flat (2D) or fully three-dimensional (3D) structures, 2.5D microstructuring enables the fabrication of complex, modulated topographies where each point on the surface can have a unique, pre-defined depth. This is achieved by utilizing the pulse-on-demand capabilities of the latest femtosecond laser sources.

Here, a 2.5D surface is defined as a modulated surface described by a

2D matrix of depths. This experimental research may open a new window in femtosecond laser microstructuring by introducing a 2.5D complex surface microstructuring concept that improves processing precision and throughput for surface structuring with minimal thermal damage to the material. The laser pulse-on-demand (PoD) method enables the creation of complex patterns by fabricating biomimetic shark skin in a single scanner pass by utilizing the dynamic modulation of laser repetition rates.

This experimental technique demonstrated up to 10 times increase in processing throughput compared to the standard laser structuring. PoD laser operation mode is the most efficient among all of the Laser-based surface structuring techniques, where the laser beams traverse over the material to be structured. PoD mode makes optimal utilization of the scanning system, though it is typically used to ensure equidistant pulse positions on the material and precisely timed laser On-Off switching. Calibration and ablation scaling experiments were undertaken on 5 different materials, including semiconductors, metals, and dielectrics (polished copper and 1.4301 type stainless-steel, acrylic glass, soda lime glass, and silicon wafer). The proof of the new concept was materialised by fabricating a biomimetic shark skin pattern in a single scanner pass, resulting in a 2D-periodic complex surface structure. Their concept employed an input of a grayscale image to define the desired depth distribution on the material.

It employed the PoD mode to modulate the laser repetition rate, enabling precise fabrication of the target structure. Surface texturing was achieved utilizing an Open Bench Laser processing system built with Industrial grade equipment typically incorporated in laser-based material processing. The green femtosecond laser beam (515 nm wavelength) was guided to x-y galvo-scanners (Newson rhothor™ 2D-MSA-A10) and focused through a 100 mm f- theta lens. For 2.5D structuring, the desired depth at a given position is encoded in an image input, as a matrix of depths - d(x, y). Assuming a linear relationship between the laser repetition rate and structure depth, the needed repetition rate is f(x, y) = kd, wherek is a constant for a particular material. This experiment may prove to be a useful technique in micro/nano manufacturing, for applications requiring textured surfaces for improved aerodynamic, hydrodynamic, and hydrophobic properties.

6.2. *Laser cleaning and ablation*

Nanosecond pulsed lasers serve a dual function by both removing existing biofouling and restructuring the substrate surface. The process involves laser-induced vaporization and ablation, which effectively eliminates fouling layers while simultaneously generating new surface topographies. These restructured surfaces often exhibit superhydrophobic behaviour, thereby resisting future biofouling [260].

6.3. *Laser cladding*

High-speed laser cladding is a surface engineering technique used to deposit alloy coatings with in-situ formed microchannels. These microchannels can act as reservoirs for antifouling agents, such as copper ions, providing sustained release and long-term antifouling protection in harsh and corrosive marine environments [261]. Laser Cladding, have the potential of considerably enhancing marine antifouling performance. By projecting high-energy lasers to melt alloy powders (like Ni60/TC_4, Cu—Fe, or Cu—Cr) onto a metal substrate, this technique allows for precisely control surface composition and texture, leading to a surface structure that can effectively resist biofouling and corrosion in harsh marine conditions. [262]. A schematic diagram of laser cladding is shown in Fig. 22. The 3D movement of the workbench can be controlled by a computer.

This process can create surfaces with the required roughness and surface energy, as well as unique features like self-grown microchannels that can store and gradually release (sustained release) antifouling agents (like copper ions), ensuring long-term sustainable protection [263]. Herong Ma et al. [261] proposed adopting high-speed laser cladding technique to fabricate copper-iron alloy capable of developing self-grown microchannels through dealloying process in a corrosive marine environment, which can actually store copper ions. The phase composition and microstructure evolution were characterized and analysed by scanning electron microscopy. Corrosion mechanism of dealloying and distribution of microchannel was studied. Their experiment showed that after being immersed in artificial sea-water for 2 months, the samples were able to form a de-ironized microchannel layer with a thickness of 350 μm, which reduced the bonding strength between corrosion products and the surface. The self-grown microchannels could store the copper ions which could be sustainably released over a lengthened period of time for prolonged antifouling activity.

In another experimental study [264], novel antifouling surfaces were fabricated by laser cladding of TC_4 (Ti_6Al_4V) and Ni60 mixed powder in various mass ratios on the surface of 316 L Stainless steel substrate plate. The results of the experiment inferred that a Laser Clad Coatings with Ni60/TC_4 mass ratio of 3:7 and by properly choosing the combination of laser cladding power and laser scanning speed, optimum wettability and antifouling performance can be achieved.

Laser cladding also produces dense, uniform coatings with superior hardness and corrosion resistance as compared to traditional methods and can be optimized to be environmentally friendly by reducing reliance on toxic chemicals [265]. However, the technique has its limitations: it is highly sensitive to process parameters such as laser speed and energy, which can affect cost of production, coating quality, microstructure, and antifouling efficiency [264], [265]. Achieving consistent nanostructures over a large ship's hull plating, managing cost and the complexity of laser equipment are additional challenges. Despite these drawbacks, laser cladding stands out for its flexibility, ability to engineer multifunctional coatings, and potential for further optimization to meet the evolving demands of maritime antifouling applications [266].

7. Conclusive inferences and future prospects

This review has systematically portrayed the progression of marine antifouling technologies, highlighting the transition from potent yet environmentally detrimental organotin-based substances, such as TBT, to a new generation of eco-friendly alternatives. The economic and environmental burdens of biofouling causing increased fuel consumption and its related expenses, elevated greenhouse gas emissions, damage to coating and hull corrosion necessitated the pressing demand for sustainable, durable and efficient antifouling coatings.

The exploration of modern strategies such as Foul Release Coatings (FRC), Protein Resistance Coatings (PRC), and the particularly interesting Bioinspired coatings, indicates a dominant trend toward altering surface topography instead of leaching biocides into marine environment. Bio-inspired approaches or biomimetics utilized by living organisms like sharks, lotus leaves, rose petals and corals to name a few, demonstrate immense potential by leveraging principles of superhydrophobicity, low surface energy, special micro/nano-topographies, and hydration layers of hydrophilic surfaces.

However, a recurring theme that emerges from this review is the challenge of translating these laboratory successes into practical, large-scale industrial applications at the shipyard/repair yard or drydock. Also, the use of high-end, expensive and delicate machineries for microtexturing in hot, humid, salt-laden atmosphere of the shipyard can pose additional challenges. Key hurdles identified to employ these methods include versatility, scalability, cost-effectiveness, long-term durability in harsh marine environments, and the environmental footprint of the manufacturing processes themselves.

Ultimately, this review concludes that no single antifouling mechanism is a panacea. The most promising path forward lies in the development of multi-functional, broad spectrum and hybrid coatings that integrate various strategies, such as physical deterrence using microtexturing and chemical resistance through modifications in surface energy, to attain durable, comprehensive antifouling effectiveness.

Based on the findings and challenges outlined in this review, future investigations and innovations in marine antifouling coatings should focus on the following essential areas:

7.1. Development of hybrid and multi-functional coating systems

The future of antifouling coatings is not in singular strategy but in synergistic combinations. Research should aim to integrate different mechanisms into a single coating system. For instance, combining the micro-texturing capabilities of laser fabrication with self-renewing zwitterionic polymers, or creating hierarchical surfaces that are both superhydrophobic and can release non-toxic, natural antifoulants. Or hybrid polymer-inorganic layered anti-corrosion coating. Or Polymer-layered inorganic composites for improving anti-corrosion barrier effect along with Graphene as an impermeable filler [267].

7.1.1. Organic-inorganic hybrid coatings for enhanced antifouling and functional performance

Organic-inorganic hybrid coatings represent a key pathway toward multifunctional antifouling systems. These coatings combine the flexibility and processability of organic polymers with the durability, stability, and bioactivity of inorganic or biopolymeric components. Such integration enables the simultaneous realization of fouling resistance, environmental compatibility, and structural robustness within a single coating matrix. Recent studies have demonstrated the versatility of these hybrid systems. For instance, Silicon-Poly (lactic acid) (Si-PLA) coatings integrate the fouling-release properties of polydimethylsiloxane (PDMS) with the biodegradability of PLA, achieving over 90 % reduction in Navicula sp. adhesion while naturally degrading in seawater [268].

Similarly, Urushiol-based polybenzoxazine/silver nanoparticle composites incorporate in-situ synthesized AgNPs within a polymeric network, providing potent contact-killing of bacteria without metal leaching and reducing biofilm formation by approximately 98 % [269]. Another innovative approach is the WLAP/PDMS fluorescent coating, which draws inspiration from coral systems and embeds waterproof long-afterglow phosphors (WLAP) in PDMS to enable photodynamic disruption of diatom photosynthesis under diurnal light cycles, resulting in more than 85 % repellence of Navicula sp. [270].

7.1.2. Multifunctional and stimuli-responsive coatings for adaptive marine antifouling performance

Building on the hybrid design philosophy, multifunctional and stimuli-responsive coatings are being developed to integrate several complementary mechanisms within a single system. These coatings aim to address the complex and dynamic challenges of marine environments by combining self-healing, antimicrobial, amphiphilic, and environmentally responsive behaviours to sustain long-term antifouling efficacy. A representative example is the self-healing poly(urea-thiourea)/tannic acid coating, where dynamic hydrogen bonding enables autonomous repair of surface scratches, maintaining antifouling integrity for over six months. The incorporation of tannic acid further imparts antioxidant and antimicrobial functionality, achieving a 99 % reduction in bacterial colonization without the use of biocides [271].

Similarly, sulfobetaine zwitterionic/quaternary ammonium copolymers demonstrate a dual-mode antifouling strategy: hydrophilic zwitterionic segments form hydration layers that repel proteins and bacteria (over 95 % reduction in *S. aureus* adhesion), while cationic quaternary ammonium groups destroy adherent microbes through membrane disruption [272] [273]. Amphiphilic polymer networks, such as PEG-PDMS systems, selectively sequester organic foulants and gradually release non-toxic hydrolyzed by products, thereby reducing microplastic adsorption by 70 % and aligning with circular economy principles [274] [275]. Furthermore, stimuli-responsive coatings including TiO_2 or azobenzene based formulations generate reactive oxygen species under UV irradiation, effectively inhibiting biofilm growth by up to 92 % [276]. Together, these developments illustrate how multifunctional coating systems can adapt to varying marine conditions through self-repair, selective interaction, and light-activated defense, offering a sustainable and intelligent approach to long-term antifouling protection.

7.2. Bridging the gap from “Lab to Shipyard”

A ship's hull has a large surface area and includes the appendages like the rudder, sea-chest and gratings, bilge keels and the bulbous bow which also needs to be coated. These areas may not be necessarily flat and may be hard to access in some cases. Research should aim to make these advanced fabrication techniques scalable, time and cost-effective for such large and intricate structures. Drydocking charges are quite expensive and may fall heavy on the shipowner if the coating takes longer than the presently available spray-painting technique. Promising technologies like 2.5D Femtosecond Laser microstructuring, which has shown to decrease processing time compared to traditional methods, should be further developed and optimized for industrial use. Further development of techniques like nano-imprint lithography, electrospinning for continuous large-area roll-to-roll application can be a critical step forward toward commercial viability.

7.3. Enhancing durability and self-healing

The delicate micro- and nanostructures that provide antifouling properties are susceptible to mechanical abrasion and environmental degradation from the strong ocean currents, waves, saline water, rubbing with the jetty fenders to name a few. The advanced manufacturing techniques like electrodeposited micro/nanostructures, nanocomposites, electroflocked surfaces and FLDW which create these patterns might encounter problems with long-term durability and adhesion to substrate under these harsh conditions, keeping in mind that a ship's scheduled drydocking interval is either 36 months or 60 months depending on the ship type, age and regulation.

Future research must prioritize enhancing the mechanical robustness and intrinsic stability of these novel coatings to withstand constant abrasion, UV radiation, and dynamic ocean forces. Research should focus on developing stronger adhesion to diverse substrates, reducing fragility and ensuring the long-term integrity of surface modifications (e.g., lubricant infusions, zwitterionic layers). Self-healing antifouling coating techniques utilize mechanisms like microcapsules, dynamic covalent bonds, and ion exchange. Advancement of these coatings for industrial application should focus on integration and collaborative effort among various fields, including chemistry, materials science, mechanical engineering, and environmental engineering. This will include not just a systematic exploration of the mechanical properties, thermodynamic qualities, and stability of materials, but also a thorough understanding of the dynamics of chemical reactions and the essential self-healing processes of the coating components [69].

7.4. Eco-friendly manufacturing processes

Techniques such as Nanocomposites leach into the ocean to deter fouling organisms. Long term environmental impact of these nanoparticles may be questionable. Also, the final coatings are designed to be eco-friendly, but the fabrication processes themselves can involve hazardous materials. Processes such as CVD, Dry and Wet Etching, Electrospinning employ hazardous chemicals. Arrangements should be in place at the shipyard/Drydock for disposing off or recycling these chemicals safely. Future technologies should include developing “green” synthesis and fabrication routes, such as using benign solvents in electrospinning, reducing energy consumption in CVD, and designing processes which generate minimal waste. Long term environmental impact of the leached chemicals also needs to be studied.

7.5. Data-driven coating designing with ML

The integration of advanced computational materials science and machine learning (ML) is transforming antifouling coating development. These approaches accelerate the discovery of new coating formulations by enabling rapid screening, predictive modelling, and optimization of performance parameters. By analyzing extensive datasets and simulating complex interfacial phenomena, ML-driven design minimizes experimental trial-and-error, reduces development time and cost, and enhances understanding of the relationships between coating composition, structure, and antifouling behaviour.

7.5.1. Performance prediction

Data-driven models are increasingly being applied to forecast antifouling performance with high precision. Deep learning classifiers, such as convolutional neural networks (CNNs), can analyze scanning electron microscopy (SEM) images to predict biofilm adhesion probability with up to 92 % accuracy, using surface topography and roughness metrics as key inputs [277] [278]. Similarly, regression-based ML models establish quantitative correlations between coating properties such as elastic modulus, hydrophobicity, and surface free energy and field performance metrics, reducing laboratory testing time by approximately 65 % [279] [280]. These predictive frameworks allow for the rational design of coating formulations with optimized antifouling characteristics before experimental validation.

7.5.2. Accelerated testing

High-throughput computational techniques complement ML prediction by expediting the validation and optimization process. Multiscale modelling methods, such as finite element analysis (FEA), simulate mechanical stresses and failure mechanisms in hybrid coating systems under realistic hydrodynamic forces, allowing identification of potential weak points such as interfacial delamination. Meanwhile, quantum level simulations based on density functional theory (DFT) or emerging quantum computing algorithms can evaluate enormous combinations of nanofillers (e.g., graphene-Al_2O_3) to predict optimal adhesion energy and interfacial stability screening up to 10^{30} potential formulations [281] [282].

CRediT authorship contribution statement

Anirban Chakraborty: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sachin Kumar Badhan:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Pankaj Sharma:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used Open AI platforms to assist with language editing, structural refinement, and improvement of clarity. After using this tool, the authors reviewed and edited the content as necessary and take full responsibility for the final version of the manuscript.

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