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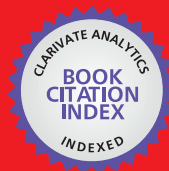International authors and editors

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Chapter

Developments and Challenges of Hydrogel Coatings for Long-Term Marine Antifouling Applications

Mengyan Nie and Koulin Chen

Abstract

As a result of the accumulation of marine organisms on submerged surfaces, marine fouling can have significant economic and environmental impacts. For example, marine fouling can increase drag and reduce the hydrodynamic efficiency of a vessel, leading to increased fuel consumption and operational costs as well as higher greenhouse gas emissions. The marine organisms attached to submerged surfaces can also induce corrosion and cause the marine structural integrity of the affected surfaces compromised, leading to increased maintenance and repair costs. Additionally, marine fouling can also pose biosecurity risks by spreading invasive species to new regions and disrupting local ecosystems. Great efforts have been made to develop effective and environmentally friendly antifouling technologies to mitigate these impacts. Hydrogel antifouling coatings have been proven effective and environmentally friendly, making them promising for practical marine applications. Here, brief overviews of antifouling mechanisms and types of hydrogel coatings are presented first. The latest developments in hydrogel antifouling coatings are categorized based on design strategies, and the limitations of these coatings are also critically appreciated with regard to their potential for practical marine applications. Finally, insightful perspectives on hydrogel coating are summarized for their use in practical marine applications.

Keywords: hydrogel, hydration layer, biofouling, coating, marine fouling, microbiologically induced corrosion (MIC), antibacterial, coating toughness, self-generating, self-healing, antifouling agent

1. Introduction

Material surfaces constantly face the threat of foreign substance adherence. When materials become covered in contaminants, their inherent interfacial properties are compromised, which would cause severe impact on their performance and even failure of engineering components. Microbial biofouling poses a significant issue in relation to biomedical devices, implants, marine structures, and food packaging materials. The formation of microbial biofilms on biomedical devices and implants

can lead to severe infections at surgical sites and even medical devices premature failure. As such, medical devices in contact with human blood must prevent protein adsorption and blood cell adhesion to avert biofilm formation and biofouling. In aquatic environments, microbes, macroalgae, and shellfish readily attach to alloys and metals, causing microbiologically induced corrosion (MIC), reducing fuel efficiency and operational performance in naval vessels, and contributing to transregional biological invasions [1].

To tackle these challenges, various antimicrobial strategies have been developed to effectively prevent bacterial attachment, broadly categorized into two main approaches: 'contact killing' which actively kills adhering bacteria and 'antifouling surfaces' that resist bacterial attachment. The approach of contact-killing often leads the killed bacteria and debris to accumulate on the surface, thereby compromising the long-term antibacterial performance of the system or the effective surface regeneration strategies needed. The antifouling surface approach mainly relies on surface modification strategies to form antifouling coatings or to produce specific surface morphologies [2]. Among current antifouling coatings, hydrogels comprising 3D networks of soft and wet materials are more promising due to their high antifouling performance and environmental friendliness. In this chapter, the working mechanisms of hydrogel antifouling coatings are briefly overviewed first, and then different types of antifouling hydrogels are critically appreciated with their limitations identified and mitigation strategies proposed. In the end, the perspectives on hydrogel antifouling coating systems are presented to address the remaining challenges for practical marine applications.

2. Antifouling mechanism of hydrogels

Due to a variety of amino-acid residues and conformation flexibility, proteins could adsorb onto nearly any material surface via noncovalent interactions, such as hydrogen bonds, electrostatic and ionic interactions, and hydrophobic interactions. Cells do not directly attach to any substances, rather they interact with the materials via the adsorbed proteins. The conformation of the adsorbed proteins dictates how the cells respond (e.g., adhesion, proliferation, differentiation, etc.). In order to prevent protein adsorption and bacterial attachment, two strategies are commonly used to fabricate antifouling coatings—to make the surface either strongly hydrated or hydrophobic. For example, the perfluorinated surfaces are usually super-hydrophobic and oleophobic, exhibiting good antifouling performance because of low-affinity interactions between most molecules and the superhydrophobic surface. By contrast, the hydration layer would form a physical and energy barrier to prevent molecule adsorption. A wide range of molecule systems with hydrophilic or ionic groups that can form strongly hydrated layers have been employed to fabricate antifouling surfaces, such as poly(ethylene glycol) (PEG) and its derivatives, zwitterionic materials, peptides, polysaccharides, and other polymers [3].

Hydrogels are composed of hydrophilic polymer networks. Their super-hydrophilic nature allows them to absorb significant amounts of water molecules into their 3D networks, forming a highly hydrated layer on their surface that prevents the adhesion of proteins or microbes. For an organism to attach, it must penetrate this hydration layer, requiring additional energy and thus reducing the likelihood of attachment [4, 5]. Moreover, the swollen state of hydrogels imparts soft and highly elastic properties, deterring most marine organisms that prefer to adhere to rigid surfaces. Consequently, hydrogels exhibit excellent resistance against proteins, marine

bacteria, green algae spores, and barnacle larvae. They are also nontoxic, highly elastic, and inert to bio-macromolecular adhesion.

Hydrogels, including polyhydrophilic and zwitterionic polymers, exhibit different mechanisms for forming their hydration layers. Hydrophilic materials leverage hydrogen bonding while zwitterionic materials utilize stronger ionic solvation. Resistance to protein adsorption correlates positively with the strength of surface hydration, which is primarily determined by the material's physicochemical properties (i.e., molecular weight and surface chemistry) and surface accumulation (i.e., film thickness, packing density, and chain conformation). In addition to surface hydration, chain flexibility plays a crucial role in protein resistance, especially for long-chain polymers. For instance, UV-initiated thiol-ene cross-linking chemistry was utilized to prepare PEG hydrogel coatings with different structural compositions by varying PEG length, vinylic end group, and thiol cross-linker [6]. The antifouling efficiency of long-chain PEG outperformed that of oligo(ethylene glycol) coatings. As proteins approach the surface, the compression of polymer chains due to entropy reduction leads to steric repulsion, resisting protein adsorption, and marine bacteria settlement. While most water-soluble polymers can reduce protein adsorption to some extent, optimal antifouling capabilities are achieved only under the combined effects of surface hydration and steric repulsion. It is speculated that the hydration layer plays the main role in the resistance against protein adsorption if chain flexibility is limited, whereas both chain flexibility and the hydration layer are important if chain flexibility is significant [4].

3. Types of hydrogels used for antifouling coatings

3.1 Polyhydrophilic polymer hydrogels

Several low- or nonfouling polyhydrophilic materials, including poly(ethylene glycol) (PEG, sometimes termed as polyethylene oxide, PEO), polysaccharides, and polyamides, share common structural and chemical properties—hydrophilicity, electrical charge neutrality, and the presence of hydrogen-bond acceptors/donors [4].

PEG and its derivatives are the most widely used antifouling materials due to the advantages of high solubility in water, superior biocompatibility, and nontoxicity. Since the 1970s, they have been utilized to modify material surfaces for antifouling coatings because of their strong antifouling tendencies toward cells and proteins. Due to their bulky volume, high hydrated chain mobility, and steric repulsion, PEGylated materials effectively reduce cell adhesion and protein adsorption [7]. The higher the degree of polymerization, the better the antifouling effect is. Ekblad et al. [8] have demonstrated that hydrogel coatings containing polyethylene glycol are highly effective in inhibiting the settlement of a wide range of fouling organisms in marine and freshwater, showing excellent antifouling properties with regard to settlement and removal. However, their widespread use is hindered by poor mechanical performance and brittleness upon dehydration [9, 10]. Furthermore, PEG undergoes oxidative degradation when exposed to oxygen, elevated temperatures, or light [11, 12], and the degradation process is significantly accelerated when ethylene glycol segments come into direct contact with a transitional metal catalyst such as gold, in the presence of oxygen and higher temperatures [13]. The oxidative degradation would make the PEGylated surface unstable and diminish their antifouling properties, and thus limiting their long-term applications. For example, PEG brushes lose their antifouling capabilities when temperatures reach 35°C, limiting their long-term resistance to protein fouling [14].

3.2 Zwitterionic polymer hydrogels

Compared with PEG and its derivatives, zwitterionic polymer materials, such as carboxybetaine (CB), sulfobetaine (SB), and phosphorylcholine (PC) demonstrate greater oxidative resistance and hydrolytic stability, and have been explored extensively as promising alternatives to PEG derivatives in developing antifouling surfaces. Zwitterionic polymers, such as polybetaines and polyampholytes, contain both positive and negative charges equally within their structure. Unlike nonionic hydrophilic polymers (e.g., PEG) that form hydration layers through hydrogen bonding, zwitterionic polymers can form a more stable and thicker hydration layer on the surface via electrostatic interactions, tightly binding water molecules through more effective and stable ionic bonds (as seen in **Figure 1**) [15], which reduce electrostatic interactions with protein molecules and minimize protein adhesion, yielding superior antifouling performance. In addition, the electrostatic interactions between water modules and dipoles present in the zwitterionic polymer chain are stronger and less sensitive to temperature than hydrogen-bonding interactions along EG chains, thus as-induced hydration layer more stable at higher temperatures (e.g. body temperature).

A key factor in the nonfouling properties of zwitterionic polymers is to control the uniform distribution of surface charge and to achieve surface charge neutrality (**Figure 2**), guiding the design of novel, fouling-resistant zwitterionic materials. Balanced charge and minimal dipole moments are crucial for enhancing the hydration capacity of the outermost layer through electrostatic interactions [16–20].

However, zwitterionic polymers swell in aqueous media, leading to poor adhesion to surfaces. Therefore, to create stable zwitterionic surfaces, extensive surface modification and covalent bonding techniques are required. Moreover, external conditions such as pH, ionic strength, and temperature significantly influence the antifouling performance of zwitterionic materials. All these factors may limit their ultimate usability in industrial applications [21].

Based on their negatively charged groups, polybetaines are categorized into sulfobetaine (SB), carboxybetaine (CB), and phosphobetaine (PB). They can be considered biomimetic molecules due to their structural similarity to natural molecules. The structure of SB is analogous to taurine, a sulfur-containing nonprotein amino acid widely present in many animals [22]. CB resembles glycine betaine, a natural compound used in humans for osmoregulation [23]. PB is homologous to the hydrophilic
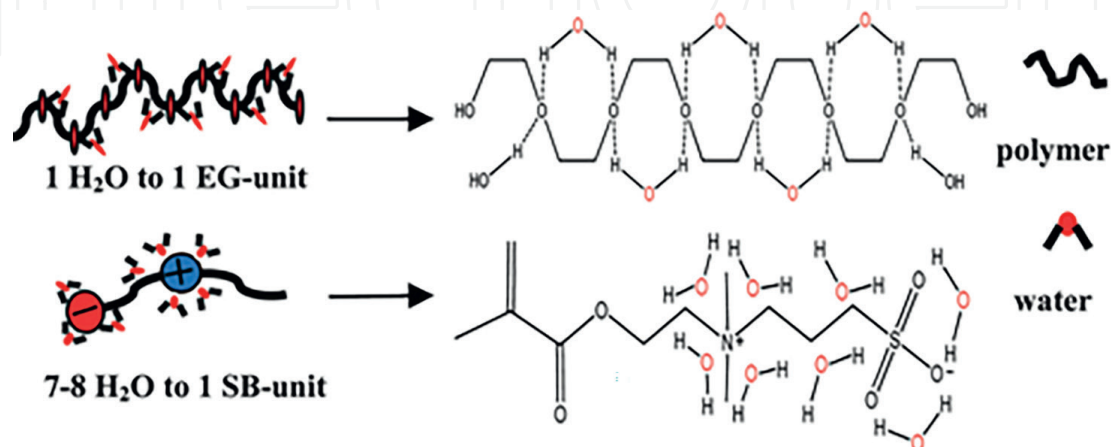

Figure 1.
Comparison of the hydration of poly(sulfobetaine methacrylate) (PSBMA) and poly(ethylene glycol) (PEG) [15].
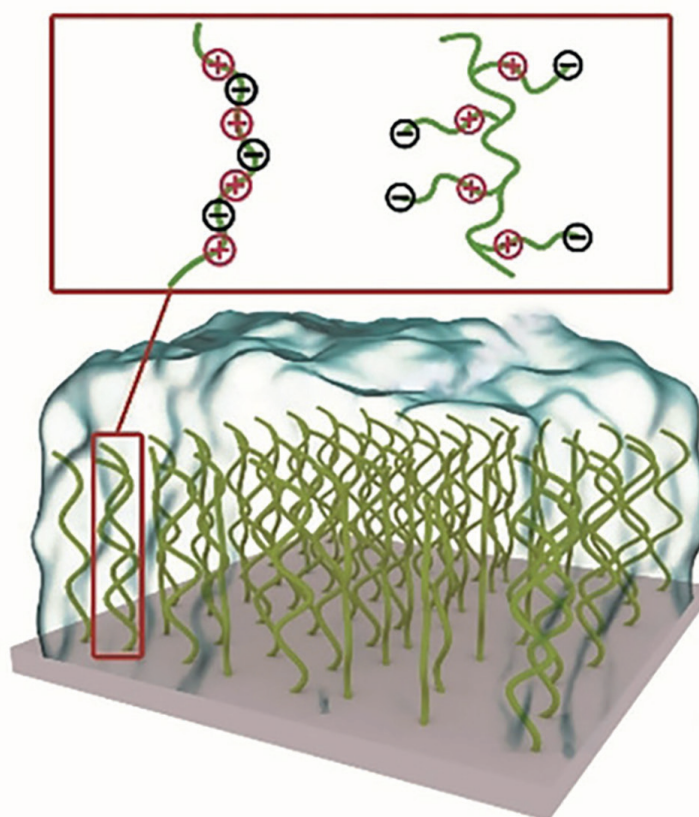
Figure 2.
The uniform distribution of surface charge of polybetaines and polyampholytes [16].

portion of phospholipids, which are major components of cell membranes [24]. However, due to high production costs, PB-based polymers have limited their applications for antifouling coatings. In contrast, SB and CB monomers are cost-effective in production. Especially, SB can be easily prepared, and the antifouling performance of polysulfobetaine is unaffected by the medium solution pH level. CB monomers are biocompatible and can be further modified to enhance their antifouling performance. Therefore, current antifouling coatings primarily utilize SB and CB [25]. Karthäuser et al. [26] synthesized a set of poly(sulfobetaine methacrylate)s (PSBMAs) to study the relationship between their structure and antifouling performance. The spacer groups, either separating the zwitterionic units from the polymer backbone or the cationic from the anionic charges, were systematically varied to explore its effect on the resistance against nonspecific protein adsorption and the accumulation of single species of marine biofouling organisms. It was revealed that the antifouling performance of PSBMAs coating could be optimized via the design of the betaine-to-backbone spacers. The shorter the ethylene spacer, the higher protein resistance is achieved. Moreover, a shorter spacer between the oppositely charged ionic groups of the zwitterionic moiety effectively favors the removal of tested fouling organisms.

In addition to polybetaines, polyampholytes represent another class of materials that are structurally similar to polybetaine polymers. These polymers achieve uniform charge distribution and charge neutrality primarily through the equimolar and homogenous pre-polymerization mixture of two monomers bearing opposite charges. Ampholytic components are notably amenable to functionalization, offering broader chemical diversity and greater flexibility in molecular design. Yeon et al. [27] synthesized an ampholytic dopamine derivative, ZW-DOPA, which contains both catechol and amine
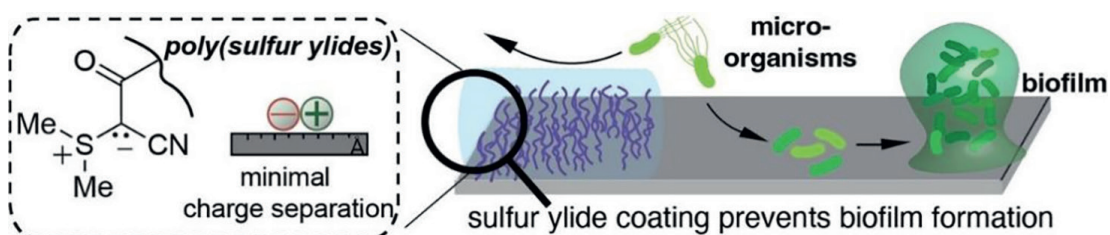
Figure 3.
Illustration of poly(sulfur ylides) coatings for preventing adsorption of biomolecules and microorganisms [29].

functionalities. Coatings based on ZW-DOPA demonstrated enhanced resistance to adhesion by marine diatoms. Furthermore, Liu et al. [28] developed a new subsurface-initiated atom transfer radical (SIATR) polymerization technique with sulfobetaine methacrylate and 3-sulfopropyl methacrylate potassium salt as monomers to fabricate ampholytic copolymer brushes, which demonstrated significantly enhanced stability of the ampholytic polymers and promising candidate for long-term antifouling coatings in marine environment. Berking et al. [29] explored a new class of zwitterionic polymers, specifically poly(sulfur ylides), which effectively inhibit the adhesion of biomolecules and pathogenic bacteria. It is also noteworthy that minimal charge separation exists in these new zwitterionic polymers (as seen in **Figure 3**), which agrees well with the favorable shorter spacer effect observed by Karthäuser et al. in [26], providing insightful guidance for the development of better zwitterionic polymers antifouling coatings.

Zhang et al. [30] also developed zwitterionic hyaluronic acid-based hydrogels via UV light-free thiol-ene click chemistry reaction, which exhibited excellent antifouling properties and good cytocompatibility and were well suitable for 3D cell encapsulation.

4. Strategies for improving the antifouling performance of hydrogel for marine applications

While the hydrophilic surfaces of hydrogels help prevent fouling by reducing the adhesion of proteins and microorganisms, their antifouling applications are still limited by unsatisfactory antimicrobial properties. The hydration layer of zwitterionic hydrogel coatings is sensitive to pH, ionic strength, and temperature of the exposed environment, which could significantly influence antifouling behaviors of zwitterionic coatings and affect protection naval vessels from biofouling when operating in different locations or seasons. Furthermore, some hydration layer-based coatings may detach or de-graft from the surfaces due to the hydrolysis of siloxane, amide, or ester bonds or cleavage of Au–S or oxidative degradation of PEG in the hydration layer. Various approaches have been developed to improve the mechanical, durability, and antifouling performances of hydrogel coatings for long-term applications in marine environments.

4.1 Enhancing adhesion to substrates via surface grafting or synergistic multimodal hydrogen bonding

It remains challenging to stably and conveniently deposit hydrophilic polymers densely and homogeneously onto various surfaces. Especially in marine antifouling, large-scale applications of hydrophilic polymer coatings can lead

to problems, such as low adhesive strength, uneven surface coverage, and short lifespan. Effectively anchoring PEG to material surfaces poses a significant challenge. Various methods, including physical adsorption [31], graft polymerization [32, 33], covalent coupling [34, 35], and plasma treatment, have been employed. For example, Kim et al. [36] synthesized a series of stable PEG-based peptides (PEGtides) hydrophilic coatings via anionic ring-opening polymerization of functional epoxy monomers like catechol and lysine, leveraging catechol–amine synergy and diverse hydrogen bonding for strong adhesion (as seen in **Figure 4(a)**). Wang et al. [37] achieved the strong adhesion of catechol-modified four-arm polyethylene glycol hydrophilic antifouling coating onto various types of materials surfaces by grafting dopamine onto the ends of four-arm PEG (4A-PEG-COOH)
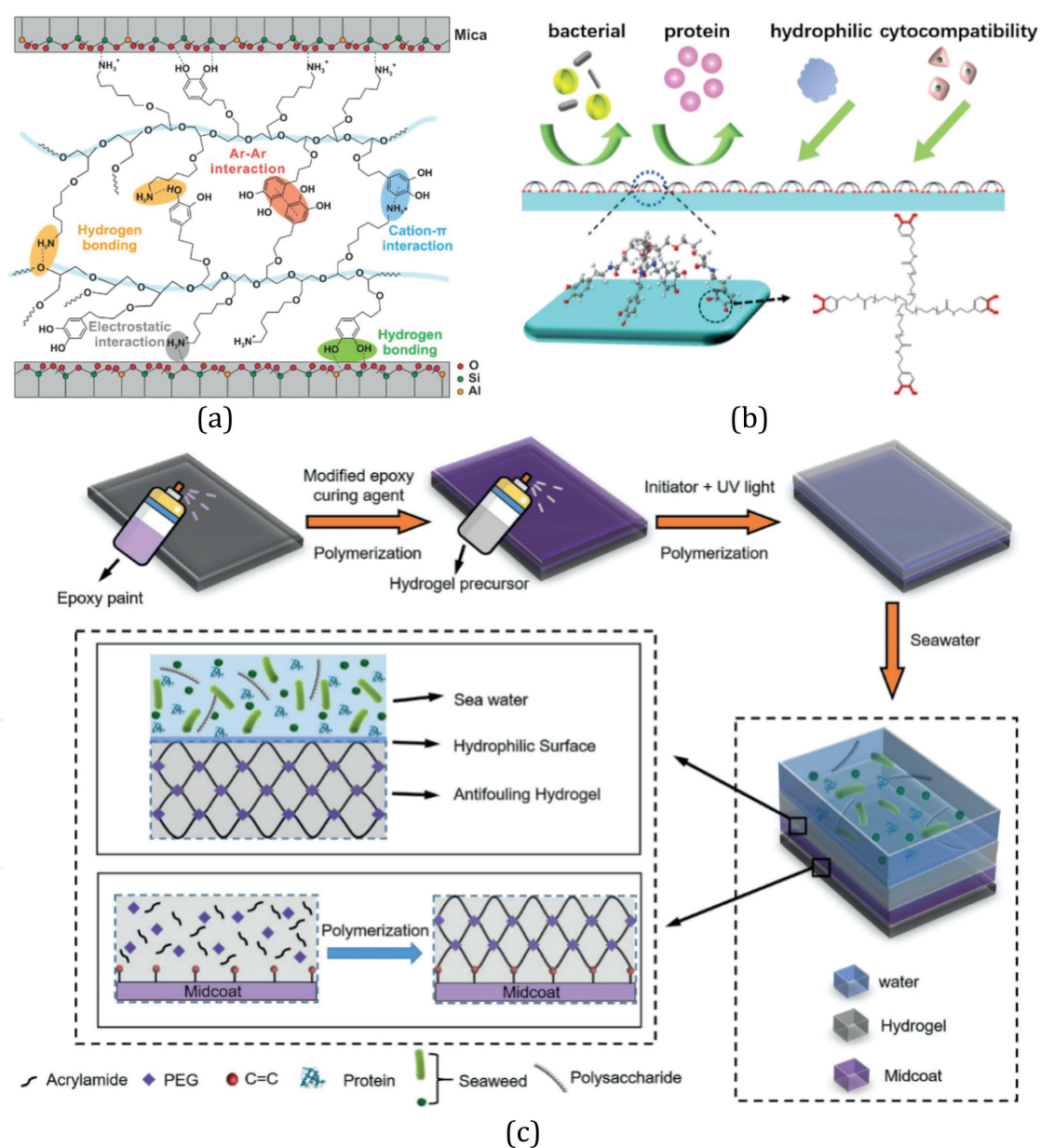

(a)

(b)

(c)

Figure 4.
Schematic diagrams of (a) the overall adhesion and cohesion mechanism of the PEGtides developed in [36], (b) 4A-PEG-DA coating in [37], (c) covalently bonded interlayer introduced between the antifouling hydrogel and substrate surfaces [38]. In (c), a layer of mid-coat is used to mediate the binding of the hydrogel layer to various surfaces. Covalent anchoring groups are used to establish strong adhesion of the hydrogel layer to the mid-coat.

(as seen in **Figure 4(b)**) through amidation reaction. Zhu et al. [39] selected an ethyl α-cyanoacrylate (ECA) adhesive that maintains a robust bond between the polyvinyl alcohol (PVA)-glycerin gel and the substrate through several dehydration/rehydration cycles, thus preserving its antifouling efficacy with excellent thermoplastic and mechanical properties. PVA-glycerol hydrogels significantly inhibit the settlement of the barnacle Balanus albicostatus. Yang et al. [38] introduced an epoxy resin interlayer (mid-coat as called in **Figure 4(c)**) in hydrogel coatings to facilitate strong hydrogel attachment to various surfaces. The strong adhesion of the hydrogel layer to the mid-coat was achieved via the formation of strong covalent bonds between them. Despite covalent bonding, the hydrogel layer provided a hydrophilic surface, thus maintaining outstanding antifouling performance.

4.2 Introducing nanomaterials for nanocomposite antifouling coatings

Some research groups have investigated the antifouling performance of organic/inorganic hybrid composite materials by mixing inorganic fillers at the nano- or micron-scale. Adding micron- or nano-sized fillers can enhance the toughness of the coating, and formation of nanocomposites can significantly improve mechanical properties of the hydrogel coatings. Liu et al. [40] first functionalized multiwalled carbon nanotubes (MWCNTs) with poly(sulfone) (PSf) and sulfobetaine methacrylate (SBMA) to produce amphiphilic and protein-resistant nanocomposite films and membranes. Wang et al. [41] later prepared PSf nano-hybrid membranes enhanced with functionalized MWCNTs with PEG as the dispersion phase, and as-prepared hybrid membranes showed better hydrophilicity and excellent antifouling properties while maintaining excellent tensile strength. Carbon nanotubes, with their excellent mechanical properties, high surface area, and good hydrophilicity, have become an ideal component for enhancing mechanical properties and increasing the porosity of composite membranes.

Ashraf [42] developed a strong and uniform nano-CuO incorporated PEG hydrogel coating over polyaniline-modified polyethylene aquaculture cage nets and observed a significant reduction in fouling over three-month field tests. Tian et al. [43] prepared a series of hybrid antifouling coatings consisting of silicone elastomer and nanocomposite hydrogel embedded with silver nanoparticles (AgNPs). The field tests in the South China Sea demonstrated that the hybrid coatings with nanocomposite hydrogel exhibited good antifouling performance regarding antialgae properties (as shown in **Figure 5**).

Zhang et al. [44] developed a cellulose-based hydrogel with integrated copper oxide nanoparticles, where $Cu_2O@CuO$ nanospheres were in-situ deposited onto the cellulose hydrogel framework. This method ensures better distribution and strong binding between the nanospheres and the hydrogel. The cellulose hydrogel exhibited not only antifouling properties due to the hydration layer on its surface but also enhanced mechanical strength, making it more durable. Li et al. [45] developed nanocomposite hydrogel coatings containing 3D porous Cu_2O nanoparticles, redox gel, and reduced graphene oxide, and observed excellent, stable, and long-lasting bactericidal performance with regard to mussel and barnacle adhesion. Instead of Cu_2O nanoparticles, Xiong et al. [46] dispersed CeO_2 nanorods into a polyzwitterionic hydrogel PVA-P(SBMA-AM) via a simple one-pot method and achieved outstanding antifouling performance, which can sustain for over 6 months in a real marine environment. The highly efficient antifouling is due to a dense hydrated layer formed on the surface
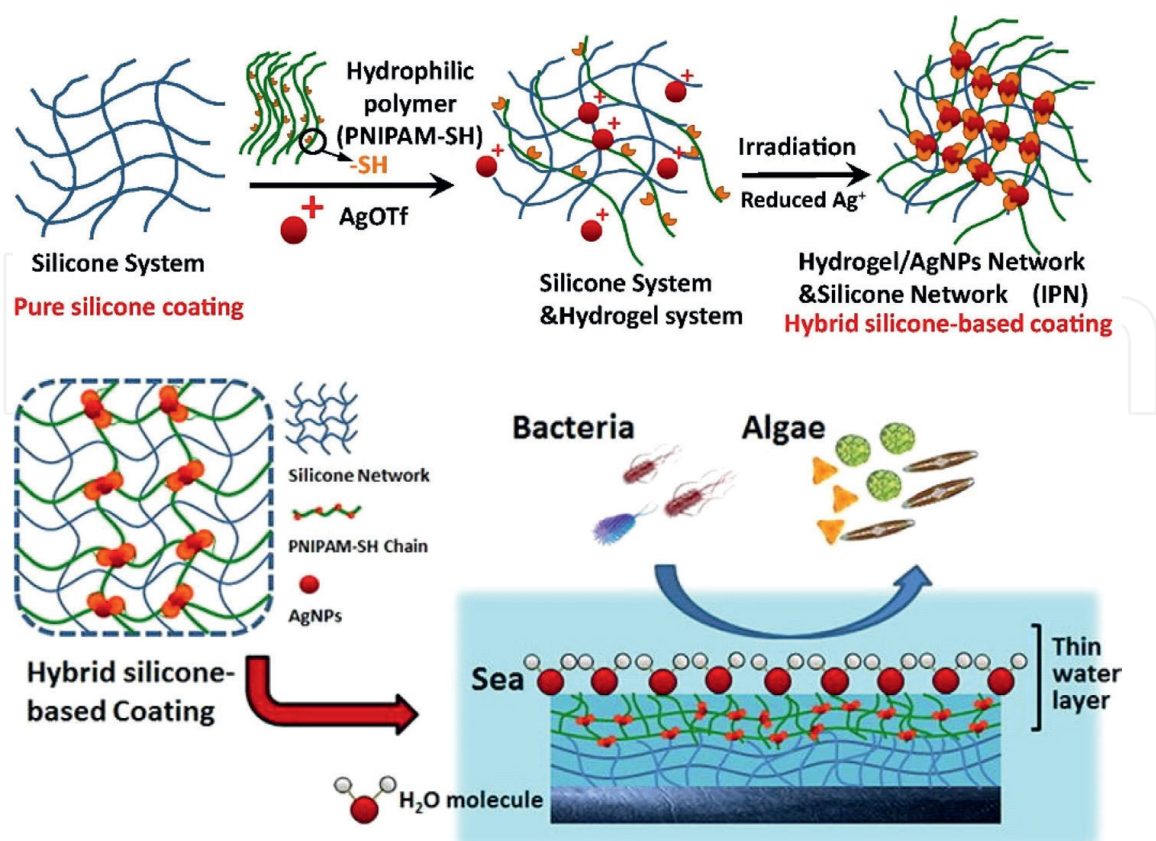
Figure 5.
Schematic illustration of the formation of the pure silicone film and the hybrid coatings (upper) and antifouling performance (lower) [43].

by the super-hydrophilic polyzwitterionic hydrogel and its subsequently excellent broad-spectrum antiadhesion behavior. CeO_2 nanorods dispersed in the hydrogel also have highly efficient bacterial-killing performance. Synergistic work between the bacterial killing of CeO_2 nanorods and antiadhesion of the polyzwitterionic hydrogel leads to its significantly improved marine-antifouling performance. Very recently, Hu et al. [47] employed $Al(OH)_3$ nanoparticle as a physical cross-linker to construct a soft antifouling polyacrylic acid (PAA)/PSBMA hydrogel coating with high toughness and low swelling through dynamic coordination bonding and plentiful hydrogen bonds.

Wei et al. [48] synthesized spindle-shaped calcium carbonate-chitosan/poly (vinyl alcohol) (SCC/PVA) hydrogels, inspired by the characteristics of good mechanical strength and self-cleaning capability of seashells. These hydrogels, containing 1–2-μm-sized spindle $CaCO_3$ particles which are well dispersed within the matrix, demonstrated stable underwater superoleophobicity, remarkable mechanical strength (with compressive strengths up to 25 MPa for SCC/PVA-3), and long-term antibiofouling performance (up to 180 days testing period) against typical fouling organism in marine environment.

Due to their high specific surface area, nanoparticles exhibit a strong tendency to agglomerate, which can negatively impact the mechanical properties of the hydrogels. Although numerous methods have been employed to modify nanoparticles to reduce their aggregation, using excessively modified nanoparticles in hydrogels can still lead to aggregation and decrease the mechanical properties of the hydrogels. Therefore, the optimal dosage of nanoparticles should be thoroughly investigated, and further developments in nanoparticle modifications should be pursued to enhance their

dispersion. Furthermore, the aforementioned metallic nano-fillers as fungicides or bactericides, such as AgNPs, Cu_2O, CeO_2, and $Al(OH)_3$, are hazardous to marine ecosystems if overused, and should be replaced by some environmentally compatible materials (e.g., calcium carbonate, chitosan, or their analogs).

4.3 Introducing double-network structure to toughen hydrogels

The mechanical properties of single network (SN) antifouling hydrogels are generally poor. For example, single network poly(sulfobetaine methacrylate) (PSBMA) hydrogel has a low fracture strain of 74.19 ± 4.27% and a weak maximum compressive stress of 0.191 ± 0.019 MPa. The compressive stress and fracture strain of another zwitterionic single network poly(carboxybetaine methacrylate) (PCBMA) hydrogel are 0.531 ± 0.058 MPa and 69.88 ± 1.93%, respectively [49]. According to the literature [43, 46, 50], introducing double network (DN) structures can effectively strengthen hydrogels and improve their long-term antifouling performance in harsh marine environments, as demonstrated in **Figure 6**. Typically, DN hydrogels consist of a rigid network that breaks easily to dissipate energy and a flexible network that enhances the tensile properties of the hydrogels, achieving a balanced state of strength and toughness [51].

Chen et al. [52] designed a new type of hybrid physically-chemically cross-linked agar/polyacrylamide (PAM) double network hydrogel with desirable/balanced mechanical properties by varying the network-forming parameters. Under optimal
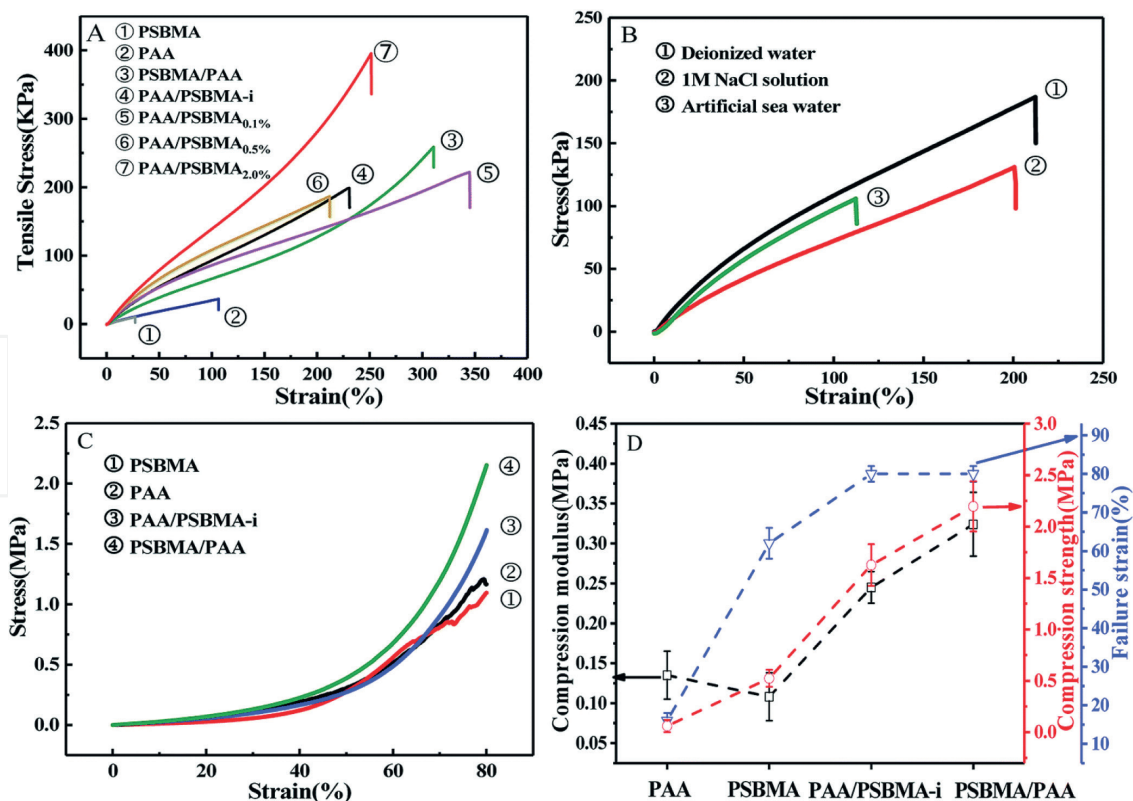

Figure 6.
(a) Tensile stress–strain curves for single-network (PAA and PSBMA) and double-network (PAA/PSBMA and PSBMA/PAA) hydrogels in deionized water. (b) Tensile stress–strain curves for double-network PAA/PSBMA$_{0.5\%}$ hydrogel under deionized water, 1 M NaCl solution and artificial sea water. (c) Compressive stress–strain curves for PAA, PSBMA, PAA/PSBMA-I, and PSBMA/PAA hydrogels. (d) Compressive properties of single- and double-network hydrogels [50].

conditions, agar/PAM DN hydrogels achieved the greatest tensile stress of approximately 3.3 MPa at a failure strain of *ca*. 2400% and the highest tensile strain of 3700% at a failure stress of 2.8 MPa, comparable to the chemically cross-linked DN hydrogels. Agar/PAM hydrogels also exhibited excellent antifouling properties by strongly resisting protein adsorption, cell adhesion, and bacterial attachment, as well as the free shapeable property to form any complex shapes.

Jiang et al. [53] prepared double network hydrogel by copolymerization of different ratios of [2-(methacryloyloxy) ethyl] trimethylammonium (TMA) and 3-sulfopropyl methacrylate (SA), followed by incorporation of a second polyacrylamide (PAM) network. Compared with the single network hydrogels, the elastic modulus, maximum compressive stress, and strain of the DN hydrogels measured by compression tests were enhanced greatly with a second PAM polymer network incorporated. It was also observed from protein adsorption and algae attachment tests that the negatively charged hydrogels showed better antialgae fouling performance than the positively charged and neutral DN hydrogels.

Great efforts have recently been made to develop double-network hydrogel for biocompatible or environment-friendly antibacterial coatings for long-term real applications in biomedical devices and naval vessels. **Table 1** summarizes some innovative approaches reported by far [46, 50, 52–62] for double network hydrogel coatings which show promise for long-term antifouling applications in harsh marine environments, especially for naval assets and reported in the past 5 years. Various interaction modes within and between networks are explored to enhance mechanical properties or to introduce additional functions to prolong the antifouling service life of hydrogel coatings. For example, Zhang et al. [58] employed a simple one-pot method to prepare a hybrid ionic-covalent cross-linked double-network hydrogel. In the DN hydrogel, sodium alginate (SA) was cross-linked by Ca^{2+} ions to serve as the rigid network, while PCBAA was covalently cross-linked to act as the flexible network. This DN hydrogel exhibited excellent mechanical properties, including high elastic modulus (0.28 MPa), high tensile strength (0.69 MPa), and robust self-healing capabilities. More importantly, the hybrid cross-linked double-network hydrogel demonstrated strong resistance to nonspecific protein, cell, bacterial, and algal adhesion, showcasing outstanding antifouling performance. Li et al. [61] developed a DN hydrogel with chemically cross-linked PAM as the first network and physically cross-linked copper alginate as the second network. The introduction of copper ions (Cu^{2+}) into the alginate network endowed the hydrogel with antibacterial properties and provided better mechanical properties through stronger cross-linking between alginate and copper ions compared to traditional calcium ions (Ca^{2+}). The introduction of BTA is believed to endow the hydrogel coating with anticorrosion properties, transforming pitting corrosion into uniform corrosion, and providing unique advantages in tidal zone applications. Still using physically cross-linked sodium alginate as the second network, Xiong et al. [62] developed an ultrahigh strength and outstanding marine antifouling hydrogel coating with chemically cross-linked PVA as the first network while introducing polyhexamethylene biguanide hydrochloride (PHMB) potent fungicide. The as-developed hydrogel demonstrated a high tensile strength of 17.23 MPa and excellent antifouling effect with no attachment observed from any marine organisms on the hydrogel coating after 6 months of immersion in the actual marine environment. The ultrahigh tensile strength of the hydrogels also remained nearly the same after 6 months of immersion in the sea. As such, the as-developed antifouling hydrogels are very promising for real applications in harsh marine environments.

Hydrogels	Interactions in DN	Mechanical properties of DN hydrogel achieved	Antifouling performance	Additional functions	Ref.
Agar/Polyacrylamide (PAM)	Hybrid: H-bond (agar) and covalent cross-linked (PAM)	E = 123 kPa, $\sigma_{f,max}$ = 3.3 MPa, $\varepsilon_{f,max}$ = 3700%	Excellent in different biological media	Free-shapeable property	[52]
Agar/Hydrophobic PAM (HPAM) (via stearyl methacrylate)	Fully physical: H-bond (agar) and hydrophobically associated PAM	E = 106–113 kPa, σ_f = 0.26–0.37 MPa, ε_f = 3390–5260%, W = 7.16–9.96 kJ m^{-3}	Not tested	Self-recovery, self-healing, improved fatigue resistance	[54]
Copolymer [2-(meth-acryloyloxy) ethyl] trimethylammonium (TMA) and 3-sulfopropylmethacrylate (SA)/PAM	Hybrid ionic-covalent cross-linked	E = 2.88 MPa, σ_f = 0.432 MPa at ε_f = 13.3% for DN-7-3 hydrogel (compression test)	Excellent on DN hydrogel with TMA/SA = 1:1	N/A	[53]
Chitosan (CS)/poly-(sulfobetainemethacrylate) (PSBMA)	Hybrid ionic-covalent cross-linked	E = 500 kPa, σ_f = 2.0 MPa, ε_f = ~820%, W = 1.360 MJ m^{-3}	Excellent in vitro and in vivo with 'repel and kill' effect	Fast self-recovery, excellent fatigue resistance	[55]
Polyacrylic acid (PAA)/PSBMA	Hybrid to fully covalently cross-linked	E = ~110 kPa, σ_f = ~0.4 MPa, ε_f = ~350%	Intermediate compared with SN PAA or PSBMA	Low swelling degree, drag-reduction	[50]
CS/(N-(2-hydroxyethyl)acrylamide) (PHEAA)	Hybrid ionic-covalent cross-linked	E = 600 kPa, σ_f = 3.8 MPa, ε_f = ~700%, W = ~ 6.02 MJ m^{-3}	Excellent in vitro with 'repel and kill' effect	Excellent fatigue resistance, fast self-recovery	[56]
Sodium alginate (SA)/PHEAA	Hybrid ionic-covalent cross-linked	E = 310 kPa, σ_f = 1.32 MPa, ε_f = ~700%	Well in vitro	Self-recovery, excellent fatigue resistance	[57]
SA/polycarboxybetaine acrylamide (PCBAA)	Hybrid ionic-covalent cross-linked	E = 280 kPa, σ_f = 0.69 MPa, ε_f = ~400%, W = ~ 500 kJ m^{-3}	Outstanding for marine environments	Good self-recovery, highly biocompatible	[58]
3-(1-(4-Vinylbenzyl)-1H-imidazol-3-ium-3-yl)-propane-1-sulfonate (VBIPS)	Fully physical: Ionic and π-π interactions	E = ~60 kPa, σ_f = ~0.20 MPa, ε_f = ~450%, W = ~ 235 kJ m^{-3}	Excellent in short-term but feasible long-term via salt treatment	Self-healable in acid, pH-sensitive strength, antifreezing	[59]
Polyvinyl alcohol (PVA)/N-(4-hydroxy-3-methoxybenzyl) acrylamide (HMBA)	Hybrid H-bond and covalent cross-linked	σ_f = 3.21 MPa at ε_f = 80% (compression test)	Excellent, long-term marine antifouling	Green antifouling	[60]

Hydrogels	Interactions in DN	Mechanical properties of DN hydrogel achieved	Antifouling performance	Additional functions	Ref.
Poly(sulfonate betaine-acrylamide) [P(SBMA-AM)]/CeO$_2$ nanorod-PVA (CeO$_2$ – PVA)	Hybrid covalent cross-linked P(SBMA-AM) and H-bond cross-linked CeO$_2$ – PVA	σ_f = 2.44 MPa, ε_f = ~450%, W = 492 kJ m$^-\sigma_f$ = 27.87 MPa (compression stress)	Outstanding antifouling in real marine environment over 6 months	High-strength, highly effective long-term marine antifouling	[46]
PAM/SA-Benzotriazole (BTA)	Hybrid ionic-covalent cross-linked	σ_f = 200 kPa, W = 128 J m^{-2}	Excellent under marine tidal environment	*Anticorrosion*, long-term antifouling	[61]
Polyvinyl alcohol (PVC)/ SA-polyhexamethylenebiguanide hydrochloride (PHMB)	Hybrid ionic-covalent cross-linked	σ_f = 17.23 MPa, ε_f = 388%,	Excellent over 6 months in marine environment	Ultrahigh strength, outstanding antifouling	[62]

Notes: Elastic modulus (E), Fracture stress (σ_f), dissipated energy (W).

Table 1.
Summary of innovative approaches reported for double network (DN) hydrogel antifouling coatings.

It is noteworthy that fully physical cross-linked double-network hydrogels demonstrate some potential functions (e.g., self-healing, self-cleaning, and antifreezing) which would help utilization of the hydrogels for long-term antifouling applications in harsh marine environments. For example, Chen et al. [54] designed fully physically cross-linked agar/hydrophobically associated polyacrylamide (HPAM) DN hydrogels, which achieved excellent mechanical strength, high toughness, and notable self-healing property without any external stimuli at room temperature. As illustrated in **Figure 7**, unlike typical DN hydrogels which networks are normally held together with hybrid hydrogen-bond or ionic-covalent interactions, both networks in the designed hydrogels in [54] are physically cross-linked, whereas a hydrogen bond associated agar helix bundles as the first network are interpenetrated with the second network HPAM which are mainly associated by strong hydrophobic interactions between SDS micelles and alkyl groups of stearyl methacrylate (SMA). Fully physical cross-linked DN antifouling hydrogels were further explored by Zheng et al. [59] with a molecular engineering strategy proposed to produce zwitterionic hydrogels with high toughness and self-healing capacity. According to molecular engineering principles, a benzene group and a positively charged imidazole were incorporated into sulfobetaine (SB) monomer to produce a new monomer, 3-(1-(4-vinylbenzyl)-1Himidazol-3-ium-3-yl)propane-1-sulfonate (VBIPS), making the side chain of the VBIPS zwitterionic hydrogels more hydrophobic and strengthening the inter/intra-chain interactions. The formation of dense ionic bonds and π-π interactions between the incorporated benzene and imidazole groups, as well as dynamic nature of these interactions, increase the rigidity of the polymer chain and the interchain interactions, enhancing the tensile and fracture toughness of the hydrogel. The reversible
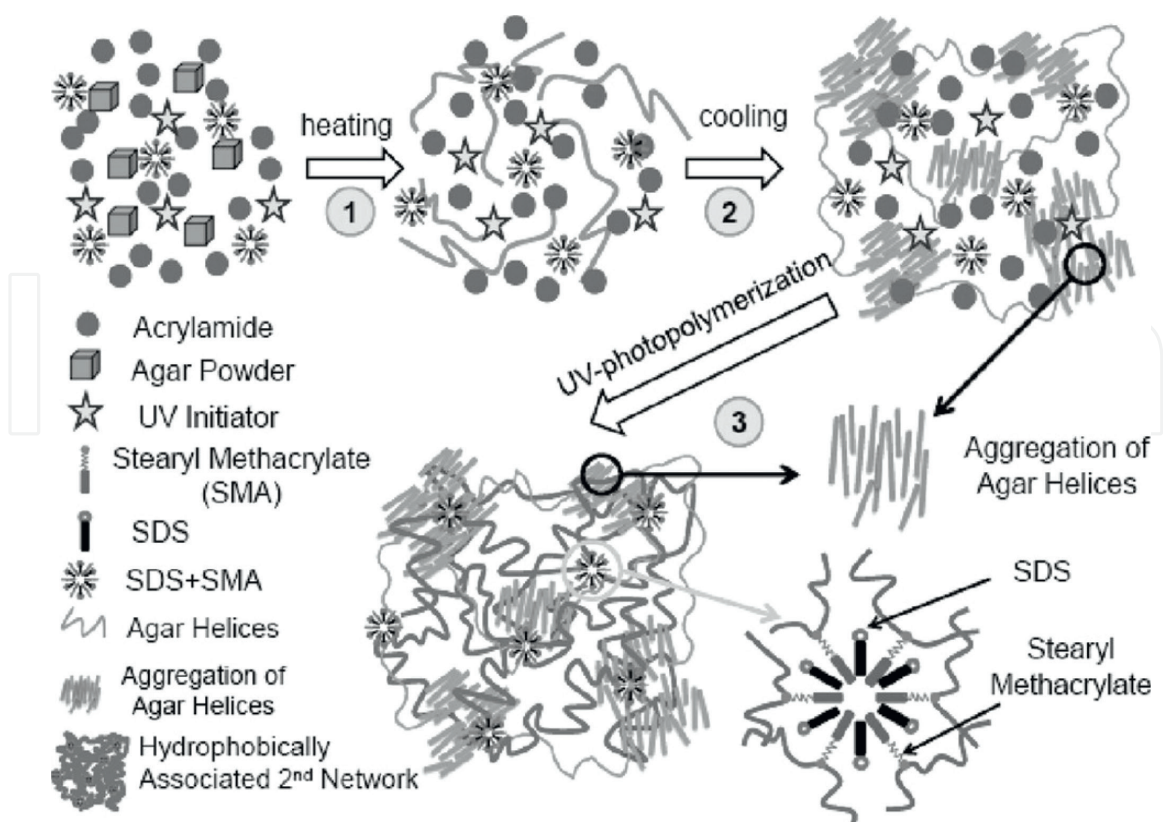

Figure 7.
Illustration of preparation and working principle of fully physically cross-linked agar/HPAM double network hydrogel [54].

and dynamic nature of ionic bonds and π-π interactions also endow the capabilities of self-healing and long-term antifouling via acid or salt treatments.

Furthermore, double network hydrogels could provide a 'repel and kill' effect by incorporating natural antifouling agents as part of networks to achieve long-term antifouling performance, as demonstrated with chitosan in [55, 56] and capsaicin analog in [60].

4.4 Incorporating natural antifoulants and their synthetic analogs into hydrogel coatings

Although the adhesion and mechanical properties of hydrogel coatings can be enhanced via the strategies discussed above, the hydrogel coatings have no intrinsic antibacterial properties and only provide an unsustainable passive biocidal effect through the formation of a hydrophilic hydration layer. This could lead to irreversible marine biofouling and even microbiologically influenced corrosion (MIC) in long-term applications as well as potential risks of marine microorganism transmission. Traditional antifouling coatings containing bactericides or fungicides, such as tributyltin, zinc ions [63], copper oxides [64–66], or TiO_2 [67], exhibit active inhibitory effects on marine organism adhesion but also pose a hazard to marine environment due to their inherent toxicity. Consequently, these coatings are prohibited for use in many countries or deemed unsuitable for practical applications. Incorporating environment-friendly natural antifouling agents or modifying existing natural ones has emerged as a promising method, as aforementioned briefly in Section 4.2. Here, we will further elaborate on recent advances in enhancing the antifouling efficacy of hydrogel coatings while incorporating multifunctional attributes to make them environment-friendly and durable in complex and harsh marine environments [68]. Natural antifoulants can be extracted from marine microorganisms [69], marine plants [70], marine invertebrates, and terrestrial sources [25]. Most natural antifoulant products are biologically extracted organic compounds, intrinsically having better biocompatibility and degradability than heavy metal-based antifouling agents. Ideal antifouling chemicals should possess a range of characteristics, including low dosage yet high efficacy, the ability to inhibit biological adhesion without toxic effects, broad effectiveness against target organisms, and a lack of negative environmental impact during degradation and mass production. Antifoulants usually disrupt their adhesion mechanisms or even kill them when fouling organisms are in close contact with antifoulant-functionalized surfaces [71, 72]. Several antifouling mechanisms have been proposed for natural antifoulants based on their roles, including protein expression regulators, oxidative stress inducers, neurotransmission blockers, surface modifiers, biofilm inhibitors, adhesive production/release inhibitors, and lethal toxicity [25]. Based on their roles and mode of operation, antifouling coatings can be categorized as contact-killing surfaces or antifoulant-releasing surfaces. In the first approach, antimicrobial groups are anchored on the surface, degrading or killing fouling organisms upon contact, while in the second approach, released antifoulants disrupt potential fouling events before attachment occurs [73].

Buzzacchera et al. [74] combined chitosan with PSBMA to develop hydrogel coatings of polymer brushes that exhibited great antifouling capabilities, significantly reducing protein fouling and preventing the activation of platelets and adhesion of white blood cells. The 'repel and kill' effect from incorporating chitosan into double

network hydrogel coatings was also demonstrated in **Figure 8** during the antifouling performance assessment in [55, 56].

Chen et al. [75] incorporated 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) into a stable double network PVA/PAM hydrogel for the first time. After hydrolysis, TMSPMA becomes a synthetic orthosilicic acid analog (SOSA) with a structure similar to orthosilicic acid. It is hard for diatoms to distinguish the SOSA from orthosilicic acid, leading them to ingest the SOSA upon attaching to SOSA-contacting hydrogel. However, SOSA cannot be utilized by diatoms to construct cell walls after intake and will disturb their reproduction activity. Therefore, SOSA is often used as an agent against diatom adhesion in the preparation of long-term antifouling hydrogel coatings with an active inhibition effect. He et al. [76] recently introduced a capsaicin analog, N,N′-((4,5,6-trihydroxy-1,3-phenylene) bis(methylene)) dipropenamide (TPA), with other monomers to prepare single network hydrogels. Combined with the antifoulant capsaicin analog TPA with the hydrophilic nature of the as-produced hydrogel, the hydrogel coatings exhibited outstanding algal inhibition and antibacterial performance over 73 days of immersion in a real marine environment. Compared with the double network hydrogel prepared with PVA and another capsaicin analog N-(4-hydroxy-3-methoxybenzyl) acrylamide (HMBA) [60], the SN hydrogel with TPA seems better in the terms of antifouling performance in marine environments, which could be attributed to different antifouling potency of capsaicin analogs used and is worthy of further investigations.

Yang et al. [77] also proposed a facile strategy to construct antifouling hydrogel coatings for long-term biomedical and marine antifouling applications by making use of the synergistic effect of highly hydrated surfaces and the active bactericidal effect from quaternary ammonium cations. The hydrogel coating was prepared with 2-hydroxyethyl methacrylate (HEMA), acrylamide (AM), dimethylaminoethyl acrylate bromoethane (IL-Br), and poly(sodium-p-styrenesulfonate) (PSS). HEMA, AM, and IL-Br copolymerize via terminal double bonds to form hydrophilic polymer chains, which provide a highly hydrophilic surface that greatly imparts antifouling properties to the hydrogel. The quaternary ammonium and sulfonic acid groups from IL-Br and PSS form ionic bonds through electrostatic interactions, while the introduced quaternary ammonium cations enhance the active bactericidal effect. Very recently, Xiong et al. developed an ultrahigh strength SA/PVA/PHMB hydrogel coating [62] and observed that the outstanding long-term antifouling effect in the real
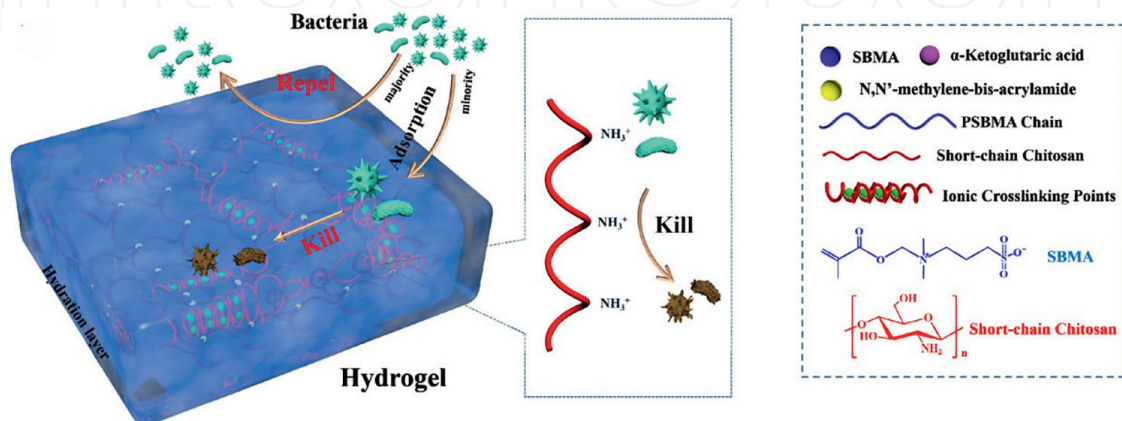

Figure 8.
Illustration of the 'Repel and Kill' effect of hybrid ionic-covalent chitosan/poly(sulfobetaine methacrylate) (CS/PSBMA) DN hydrogel [55].

marine environment was due to strong interactions between the carboxylate anions in SA and the ammonium cations in PHMB as well as the firm bonding of PHMB to the hydrogel. As-designed hydrogel coating combines both excellent mechanical properties and a highly efficient antifouling effect, emerging as one of the most promising marine antifouling coating materials.

4.5 Integration of self-generating function into hydrogel coatings for long-term antifouling performance

Despite good progress made with antifouling coatings, antifouling functions of most reported coatings are readily lost when detachments or scratches occur through physical damage and chemical degradation by water, oxygen, possible catalytic ions, particles, or even rocks and icebergs in harsh marine environments. As proposed in Section 4.1, adhesion to the substrates could be greatly enhanced via surface cross-linking or synergistic multimodal electrostatic interactions. The adhesion enhancement approaches could reduce the coating detachment to some extent but could not fully address detachment and scratch issues caused by physical damages (e.g., erosion by sand particles in seawater or collisions with rocks or marine creatures when naval vessels operate at high speeds). Consequently, it is important to develop durable antifouling coatings with self-polishing, self-generating, self-recovery, or self-healing capabilities. This is especially true when the hydrogel coatings are operated in the mode of contact-killing surfaces which incorporate antifouling or antimicrobial agents that need to be maintained or regenerated on the surfaces. In the case that antifouling agents are released from the coating onto the surface to kill fouling organisms, self-polishing is necessary to maintain an appropriate level of antifouling agents on the surface, as shown in **Figure 9** [78, 79].

At an early stage, most self-polishing coatings contain acrylic or polyurethane copolymers with biocides tributyltin or cuprous oxide (Cu_2O) [80], which degrade slowly in seawater, facilitating the release of fouling biomolecules and organisms. This allows for multiple surface renewals before re-coating is necessary. Such strategies have been extensively used on ship hulls, following significant breakthroughs with the concept of self-peeling hydrogel coating proposed by Xie et al. in [81]. The self-peeling hydrogel was prepared by mixing a polyfunctional aziridine cross-linking agent and a prepolymer copolymerized with methyl methacrylate (MMA), acrylic acid (AA), and tributylsilyl methacrylate (TBSM). The coating can be easily applied onto a surface to form a cross-linked polymer film by conventional brushing or spraying methods. When immersed in seawater, the film self-generates a thin hydrogel layer at the water-contacting surface as a result of the hydrolysis of TBSM. The as-formed hydrogel layer is hydrophilic due to hydration, thus preventing protein adsorption and microorganism attachment. The hydrogel-formation process continues after gradual corrosion and detachment of each top hydrophilic layer, which makes it promising for long-term practical applications. The same group [82, 83] further explored the approach by replacing TBSM with triisopropylsilyl methacrylate (TIPSM) to prepare the self-peelable hydrogel coatings. The field testing results over 2 months of immersion in the sea demonstrated good antibiofouling performance. It was also noted that both the formation and the self-peeling of a thin hydrated layer on the hydrogel coating surface play important roles in its antifouling properties, and there exist delicate balances between the hydrogel formation and the self-peeling rates that can be properly adjusted by the type and content of hydrolysable comonomer and the cross-linking degree. Wu et al. [78] later improved both mechanical
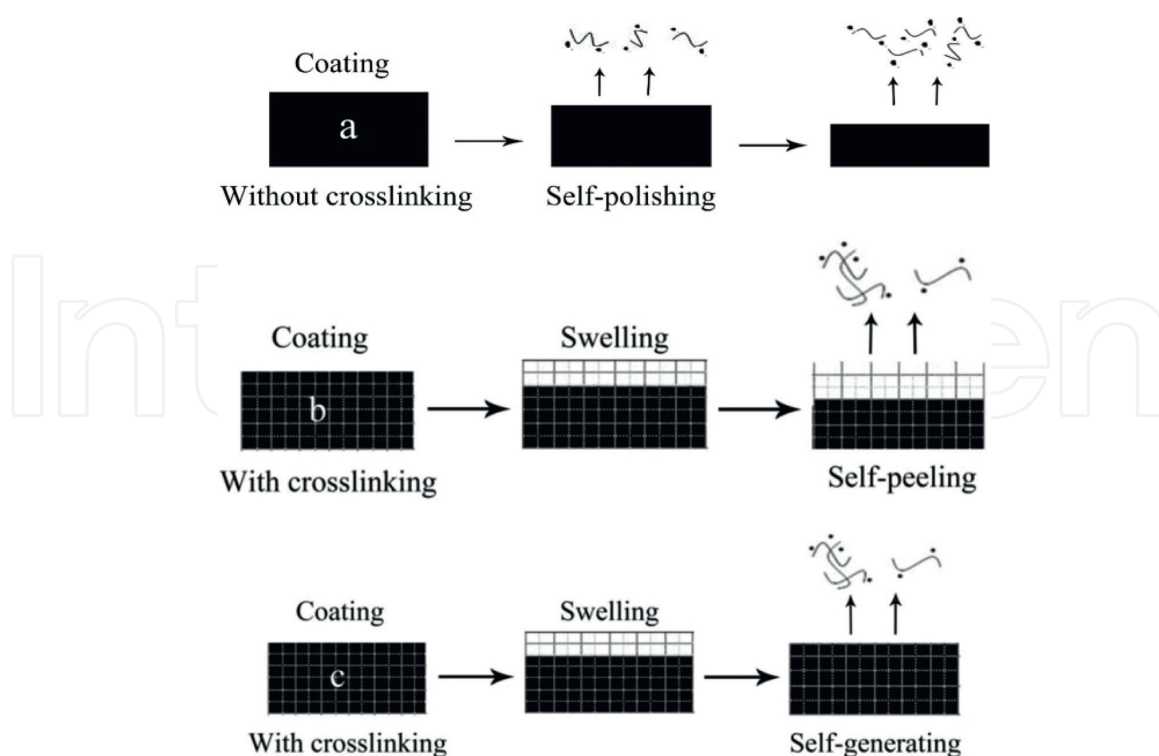
Figure 9.
Schematic of self-polishing processes of (a) uncross-linked and (b) self-peeling hydrogel coatings as well as (c) cross-linked self-generating hydrogel coatings in seawater [78].

and antifouling properties of the coatings by tailoring the used acrylamide (AM) derivatives and incorporating N,N′-[(2-hydroxy-4,5-dimethylbenzene-1,3-diyl)-dimethanediyl] bisprop-2-enamide (HDDE), a capsaicin derivative as active antibacterial agent while maintaining self-peeling and self-generating properties (**Figure 10**).

Dai et al. [84] developed a self-generating and self-renewing zwitterionic hydrogel coating with a different silyl acrylate monomer, tertiary carboxybetaine triiso-propylsilyl ethyl acrylate (TCBSA), co-polymerized with MMA and 2-methylene-1,3-dioxepane (MDO). The copolymer rapidly self-generates a zwitterionic surface due to its hydrolysis, and the hydrolyzed polymer chain can dissolve into seawater, leading to a self-renewing dynamic surface, and providing persistent fouling resistance. Moreover, the ester units introduced into the main chain make the polymers degradable, and the degradation rate is sensitive to the enzyme concentration, which further contributes to the self-renewing dynamic surfaces. Lab testing results exhibited excellent protein resistance and antifouling performance against marine bacteria *Pseudomonas* sp. and diatoms. Later the same group [85] developed a degradable hyperbranched polymer containing antifouling moieties N-(2,4,6-trichlorophenyl) maleimide (TCB-TCPM), proposing a coating capable of effectively combating marine biofouling through a synergistic mechanism. Upon exposure to seawater, the polymer surface undergoes hydrolysis, releasing antifouling agents that kill adhered microbes (attack), and generate zwitterionic groups to prevent new organisms from attaching (defense). Moreover, this coating can self-regenerate, with its degradable structure allowing for a continually renewing antifouling surface. The proposed strategy, termed as 'kill—resist—renew trinity', combines these mechanisms to provide a highly promising platform for antifouling coatings. However, its antifouling efficacy needs to be further investigated in actual marine environments for long-term applications. Alternative approaches have also been developed by incorporating
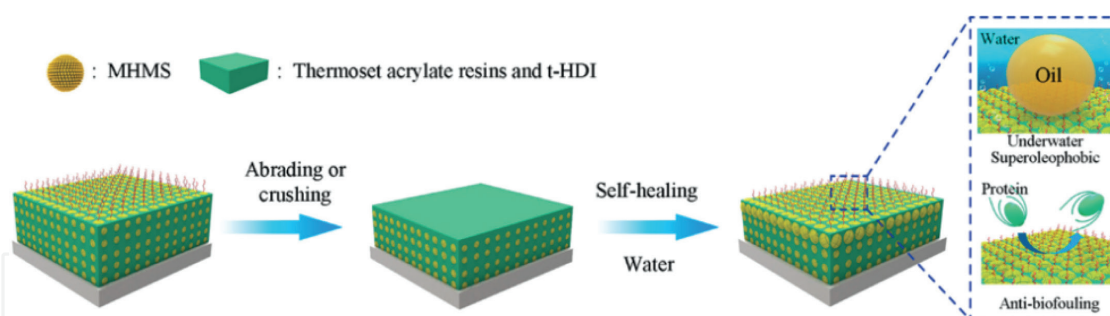
Figure 10.
Working principle of the self-repairing underwater antifouling coating [79].

nanostructured antifouling agents, such as Cu_2O [65, 86], AgNPs [87], and TiO_2 [88], into hydrogel coatings to enable self-cleaning and self-generation for sustainable antifouling in marine environments, although these approaches could raise concerns about potential metallic hazards to marine ecosystem for practical applications.

4.6 Stimuli-responsive hydrogel coatings

Stimuli-responsive coatings can swiftly and reversibly switch their surface properties based on minor environmental changes such as temperature or pH [89]. Combining this responsiveness with antifouling properties could become a valuable strategy for achieving surface regeneration. In such cases, a simple trigger (like salt, pH, temperature, solvent, light, or stress) can easily remove fouling and restore antifouling properties while addressing the concerns caused by incorporating metal oxides antifouling agents for self-regeneration discussed above.

4.6.1 Temperature-responsive antifouling coatings

Thermal-responsive polymers like poly(N-sopropylacrylamide) (PNIPAAm) combine antifouling and fouling release properties. PNIPAAm undergoes a dramatic reversible phase transition from a soluble, swollen, hydrated, and protein-repellent state below its lower critical solution temperature (LCST, 32°C), to an insoluble, collapsed, dehydrated, and protein-adhesive state above this temperature. Below the LCST, antifouling behavior is promoted by the hydration of the acrylamide groups along the polymer brush backbone, which also facilitates the release of dead bacteria. Above the LCST, the layers based on PNIPAAm collapse, causing the coating to absorb smaller proteins and bacteria while exposing antifouling parts that kill bacteria [90]. Yu et al. [91] designed a temperature-responsive switchable surface by grafting the nanopatterned PNIPAM polymer brushes and an antimicrobial quaternary ammonium salt (QAS) at the polymer-free region to achieve the function of attracting bacteria, killing bacterial, followed by releasing bacteria. Wang et al. [92] designed a hierarchical polymer architecture, which can perform the phase transition from antibacterial to antifouling upon increasing temperature from room temperature to physiological conditions at 37°C. The upper layer is a thermal-responsive bactericidal layer of poly(N-isopropylacrylamide-co-2-carboxyethyl acrylate) [P(NIPAAm-co-CEA)], and the lower layer is an antifouling layer of poly(sulfobetaine methacrylate) (PSBMA). At lower temperatures, the upper layer actively kills bacteria, while at higher physiological temperatures, the collapse of the polymer structure exposes the antifouling layer, making it cell-repellent. This dual functionality is particularly

useful for medical implants as it prevents infection while minimizing tissue irritation. However, thermal-responsive coatings are seldom reported for marine antifouling applications possibly due to temperature change seldom observed or the impracticability of adjusting environmental temperatures in most real marine applications.

4.6.2 pH-responsive antifouling coatings

pH is a suitable factor to activate a coating to switch between bactericidal and cell-repellency states, thereby preventing the formation of biofilm. The key reason for the antifouling mechanism is associated with pH variation during the metabolization of bacteria [93]. The decrease of pH in the surrounding environment due to bacterial growth acts as a trigger to release bactericidal substances. Xu et al. [94] integrated the pH-responsive strategy, self-cleaning mechanism, and 'one-step' anchoring process to develop environmentally responsive fouling release coatings. The pH-responsive switchable coating was constructed by grafting pH-sensitive poly (2-diisopropyl aminoethyl methacrylate)-b-poly(2-methacryloyloxyethyl phosphorylcholine) (PDPA-b-PMPC) and cationic polylysine (PLYS) chains with azido-modified tannic acid (TA-N3) via copper-free azide—alkyne 'click' reaction. When the pH decreases due to bacterial adhesion onto the surface, the bactericidal polymer brush coating is switched to an antifouling layer with self-defensive (fouling-release/self-cleaning) capability. The coating was found to be stable and durable over 30 days of immersion in filtered seawater or 14 days of exposure to flowing seawater.

4.6.3 Photo-responsive antifouling coatings

While pH and temperature are attractive triggers for some localized marine applications, their uses in naval vessels (e.g., ship hulls) might be limited due to difficulties in temperature and pH control within the exposed local environments. However, due to its noninvasive, inherently clean, and accessible characteristics, light could be an effective stimulus to trigger the coating function to switch reversibly between bactericidal and bacteria-releasing states. Wei et al. [95] explored a smart antibacterial surface that can switch functions in response to UV-visible light. This surface combined azobenzene (Azo) groups with a biocidal β-cyclodextrin derivative conjugated with seven quaternary ammonium salt groups (CD-QAS). When the Azo groups on the coating surface are in trans form, CD-QAS makes the coating surface strongly bactericidal, effectively killing attached bacteria. Upon UV light exposure, Azo groups switch to cis form, and the Azo/CD-QAS inclusion complexes disassociate and release dead bacteria from the surface. This reversible functional switch allows the coating surface to regenerate between killing bacteria and releasing them, which was particularly beneficial for reducing long-term biocidal activity depletion in practical applications. Li et al. [96] developed another antifouling hydrogel coating based on a photothermal antibacterial approach by introducing in-situ modified polydopamine nanoparticles (PDA NPs) with Cu NPs (PDA@Cu NPs) into a polyelectrolyte hydrogel precursor (cationic polyethyleneimine/anionic pectin, CPAP). Due to the inherent bacterial capture/killing capability of the CPAP hydrogel and the enhanced photothermal conversion efficiency of the PDA@Cu NPs, the fabricated coating exhibited highly efficient, convenient, broad-spectrum, and environmentally friendly antibacterial performance. This hydrogel shows excellent potential for antibacterial applications, demonstrating significant efficacy against common pathogens, biocompatibility, and hemocompatibility. However, its application is limited to surfaces easily accessible to light. Moreover,

a thick layer of fouling material does not allow light penetration, implying the need for frequent cleaning to maintain photoactive bactericidal capabilities.

4.6.4 Salt-responsive antifouling coatings

Salt-responsive antibacterial hydrogels have been developed for wound-healing applications. For example, Yuan et al. [97] developed a salt-responsive hydrogel with triple functions of antifouling, bactericidal, and bacterial release by combining ε-poly-L-lysine (EPL), poly(ethylene glycol) diglycidyl ether (PEGDGE), and poly(DVBAPS-co-GMA) via a one-pot method. Poly(DVBAPS-co-GMA was firstly copolymerized with monomers (3-(dimethyl(4-vinylbenzyl))ammonium sulfonate (DVBAPS) and glycidyl methacrylate (GMA), which provides antifouling and salt-responsive properties due to the presence of the salt-responsive zwitterionic monomer DVBAPS. Afterward, different functional polymers EPL, poly(DVBAPS-co-GMA), and PEGDGE were mixed with rational feed ratios to react with adjacent chains to form covalently cross-linked hydrogel. Within the hydrogel, EPL as a cationic peptide can impart certain sterilization properties while the PEGDGE with sufficient OEG groups prevents the initial bacterial adhesion effectively. Due to the presence of amine residues, the designed hydrogels were further quaternized by reacting with glycidyltrimethylammonium chloride (GTMAC) to prolong antibacterial properties. The as-prepared hydrogels demonstrated good antifouling and sterilization capabilities, and ca. 94% of the attached bacteria can be released after saline/water switching for several cycles. Fang et al. [98] investigated the antiadhesion properties of salt-sensitive purely zwitterionic hydrogel PSBMA, which was physically self-assembled due to the inter- and intra-molecular ion interactions. The PSBMA polymer was demonstrated to be intriguingly customized into a transient network with outstanding antifouling capability depending on the ion concentration. When ion concentration increases, the PSBMA hydrogel dissociated completely, endowing it as a candidate for bacterial adhesion prevention. Taken these together, salt-responsive hydrogels not only demonstrated their promising potential in wound healing management, but also a strategy to customize for seawater desalination and wastewater treatment applications in marine environments [99].

Stimuli-responsive hydrogel coatings provide valuable guidance to develop long-term and durable antifouling strategies for practical marine applications. However, great challenges remain for the large-scale applicability and durability of stimuli-response hydrogel coatings, as well as the controllability of external stimulus triggers. The multiple switches might also compromise the coating quality, thereby weakening antifouling performance and leading to fouling to build up [100]. Design strategies and the latest research advances in stimuli-responsive antibacterial coatings have been reviewed in more detail [2, 7, 101–103].

5. Conclusions and outlook

The accumulation of marine organisms causes marine fouling, which poses negative impacts on the structural integrity of marine assets and has significant economic and environmental implications. Currently, antifouling coatings represent the most effective strategy to prevent marine fouling. Especially as environmental awareness grows, marine antifouling coatings are evolving toward more effective, durable, and eco-friendly, as well as simpler to process. So far, no single polymer

coating formulation has been identified as a universal and effective marine antifouling coating strategy, and leveraging the synergistic advantages of several antifouling strategies into one multifunctional and smarter coating is highly desirable for effectively tackling marine fouling challenges. Among them, hydrogel coatings have been proven promising for practical marine antifouling applications due to their higher efficiency and the diversity of available enhancement strategies, for example, improved adhesion onto any substrates via cross-linking or multimodal electrostatic interactions, toughening via introducing nanomaterials or double network structures, eco-friendliness via integration of natural antifoulant or their analogs, and long-term durability via integration of self-regeneration or self-healing properties.

Despite the great progress made so far, considerable efforts are still needed to further enhance the antifouling efficacy and durability of hydrogel coatings. These efforts should focus on prompting their responsiveness to the changes in the exposure environment and the coating itself (e.g., surface damage/impact, pH, temperature, salinity, and light) as well as developing simplified but precision-controlled mass production technologies, which could be achieved through further development or incorporation of advanced polymerization or processing techniques (e.g., precision in-situ polymerization). For example, transforming these coatings into commercial (large-scale) applications may involve simplifying common covalent grafting methods or shifting the focus to physical adsorption techniques (e.g., layer-by-layer assembly and spray painting). Moreover, integrating smart materials responsive to environmental stimuli (such as changes in pH, temperature, and salinity [104]) could pave the way for dynamic antifouling surfaces that can actively prevent biofouling or release antifouling agents on demand.

Hydrogel coating could effectively prevent marine biofouling and even microbiologically induced corrosion. Nevertheless, the protection of the underlying metallic substrates from marine corrosion is still in demand. As illustrated in **Figure 11(b)**, the hydration layer is hydrophilic, allowing corrosive ionic species such as chloride ions to diffuse through the hydration layer and trigger marine corrosion if the underlying metallic substrates are not adequately protected or if there are cracks or porous defects within hydrogel coating. As such, in order to provide complete protection, antifouling coatings should be integrated with anticorrosion coatings via layer-by-layer structures (e.g., HVOF-deposited amorphous anticorrosion coatings as shown in **Figure 11(a, b)**) or be incorporated with suitable corrosion inhibitors (e.g., BTA inhibitor for Cu-based alloy substrates as shown in **Figure 11(c)**). More efforts should be directed toward further developing integrated antifouling and anticorrosion hydrogel coating systems to achieve comprehensive marine protection, thereby enabling their transformation for practical marine applications.

It is well known that the marine organisms attached to submerged surfaces can not only induce corrosion and cause the marine structural integrity of the affected surfaces compromised but also contribute to the biosecurity risk by spreading invasive species to new regions and disrupting local ecosystems. With further Arctic exploration and the potential increase in Arctic shipping, biofouling on vessels would pose severe threats to the fragile Arctic ecosystem. The sea ice in the Arctic shipping routes could collide with vessel surfaces and damage the surface coatings. Therefore, there are great challenges for marine protection coatings which must have high erosion resistance and antifreezing properties in addition to excellent antifouling and anticorrosion performance under subzero temperatures. Several hydrogel antifouling coatings have been reported with excellent antifreezing properties [59, 106–108], but the mechanical strength of these coating materials is normally in the range of
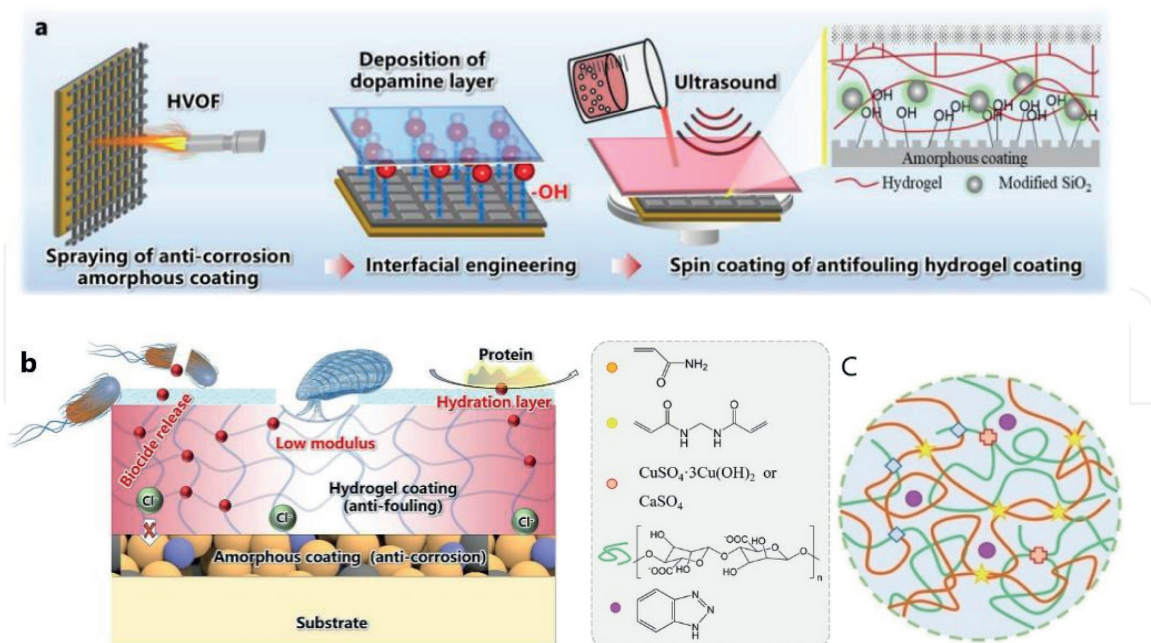
Figure 11.
Schematic illustration of the preparation process of (a) and working principles of integrated antifouling and anticorrosion functionalities of hydrogel-anchored Fe-based amorphous coatings [105]. (c) Illustration of BTA-loaded hydrogel coating [61].

20–190 kPa, which is not strong enough for sustainable and long-term marine antifouling applications regardless of anticorrosion performance. More attention should be paid to developing coatings that can completely protect Arctic shipping facilities from marine fouling and corrosion under subzero temperatures.

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