Emerging Trends in Smart Self-Healing Coatings: A Focus on Micro/Nanocontainer Technologies for Enhanced Corrosion Protection

Simpy Sanyal [1,2,3], SeonJu Park [4], Ramachandran Chelliah [3,5,*], Su-Jung Yeon [3,5], Kaliyan Barathikannan [3,5], Selvakumar Vijayalakshmi [3,5], Ye-Jin Jeong [3], Momna Rubab [6] and Deog Hawn Oh [3,5,*]

1 J&L Tech, Ansan 15618, Republic of Korea; sanyal@jnltech.co.kr
2 Saveetha School of Engineering, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences (SIMATS) University, Sriperumbudur 600124, India
3 Department of Food Science and Biotechnology, College of Agriculture and Life Science, Kangwon National University, Chuncheon 24341, Republic of Korea; sujung0811@gmail.com (S.-J.Y.); bkannanbio@gmail.com (K.B.); vijiselva10@gmail.com (S.V.); yeajin0815@kangwon.ac.kr (Y.-J.J.)
4 Metropolitan Seoul Center, Korea Basic Science Institute (KBSI), Seoul 03759, Republic of Korea; sjp19@kbsi.re.kr
5 Future F Biotech Co., Ltd., Chuncheon 24341, Republic of Korea
6 Department of Food Engineering and Biotechnology, New Campus, University of Engineering and Technology, Lahore 54000, Pakistan; rubab.momna@gmail.com
* Correspondence: ramachandran865@kangwon.ac.kr (R.C.); deoghwa@kangwon.ac.kr (D.H.O.)

Abstract: Smart self-healing coatings offer a revolutionary approach to mitigating metal corrosion, a problem with significant economic and environmental impacts. Divided into intrinsic and extrinsic types, these coatings autonomously rectify the damage. Intrinsic variants utilize reversible bonds to achieve ongoing repair, while extrinsic ones incorporate micro/nanocontainers that activate upon environmental triggers to mend micro-cracks, their efficacy dictated by the encapsulated healing agents' volume. This review dissects the rapidly evolving sector of stimuli-responsive self-healing coatings, emphasizing the progress in micro/nano container technology. It discusses the synthesis and encapsulation processes of different micro/nanocontainers and charts the transition from single to multistimulus-responsive systems, which enhances the coatings' sensitivity and functionality. The addition of multifunctional traits such as self-reporting and anti-microbial actions further broadens their industrial applicability. The review provides a succinct overview of the field's current state and future potential, envisioning a paradigm shift in corrosion protection through advanced smart coatings.

Keywords: stimulus-responsive containers; multifunctional self-healing coatings; active corrosion protection

1. Introduction

Metal corrosion is a significant issue, leading to substantial economic losses annually and adversely affecting our daily lives. One of the most efficient and convenient methods to combat this problem is through the application of anti-corrosive coatings, which serve to shield metal surfaces from degradation. The primary function of traditional anti-corrosive coatings is to act as a physical barrier, blocking the direct interaction between corrosive agents, like ions and water, and the metal substrate [1]. This method is typically referred to as passive corrosion protection due to its static nature. However, despite their initial effectiveness, these coatings are not impervious to wear and damage over time, especially under harsh environmental conditions. As these coatings age and are exposed to aggressive environments for prolonged periods, they become vulnerable to the very elements they are meant to guard against [2]. This vulnerability manifests in the form of micro-pores

and cracks on the coating's surface, which develop over time. These tiny imperfections compromise the integrity of the coating by providing pathways for corrosive ions to penetrate and reach the metal surface underneath [3].

Once these aggressive ions infiltrate the coating, they initiate a process of degradation both coating the matrix itself and the metal beneath. This degradation is not static; as the coating remains in service, these micro-corrosive sites expand, further weakening the coating's protective capabilities and leading to more severe corrosion of the metal substrate [4]. This progressive deterioration highlights a significant limitation of coatings that only offer a physical barrier: they often fail to provide long-term protection, especially in environments that are both physically demanding and chemically aggressive. Such conditions exacerbate the limitations of passive protection, underscoring the need for more advanced, active corrosion protection strategies that can adapt and respond to changing environmental conditions and prolong the lifespan of metal structures [5].

Efforts to enhance the durability and effectiveness of anti-corrosive coatings have led to significant advancements in recent years [6]. A key development in this field is the emergence of "smart self-healing coatings", a concept that has garnered considerable attention and research [7]. These coatings can be classified into two types based on their self-healing mechanisms: intrinsic and extrinsic. Intrinsic self-healing coatings possess an inherent ability to repair themselves at the molecular level. This capability stems from the breakage and subsequent reorganization of molecular chains within the coating material, enabling it to autonomously heal damage [7]. This property is an intrinsic characteristic of the material, meaning the material itself can recover from damage without external intervention. On the other hand, extrinsic self-healing coatings achieve their protective function by incorporating active agents such as corrosion inhibitors and healing substances. These agents not only reinforce the coating's physical barrier against water, oxygen, and corrosive ions but also actively repair and maintain the coating structure. When the physical barrier is compromised, these active species act to minimize corrosion reactions at the metal/electrolyte interface, effectively transforming a passive corrosion protection system into an active one [8]. In this manner, the coating's protective actions are triggered when damage occurs, enhancing its longevity and effectiveness. However, these advanced coatings are not without drawbacks. A significant limitation of active corrosion protection is the finite nature of the self-healing function—once the active species are depleted, the coating loses its self-repair capability [9].

Additionally, challenges such as poor compatibility with the polymeric matrix and potential reactions between the active species and the matrix can lead to uncontrolled release of the active agents, diminishing the coating's performance [10]. Environmental and health concerns also play a role, particularly with chromate-based coatings, which have been banned in many countries due to the toxicity and carcinogenic risks of chromium (VI).

Addressing these issues, recent research has focused on intelligent coatings based on micro/nano containers [11]. These containers, pre-loaded with active substances, are dispersed within the polymeric matrix. They are designed to respond to environmental stimuli, allowing for the controlled release of the encapsulated agents to repair and protect the coating. This approach represents a new frontier in "active corrosion protection", with a focus on designing micro/nanocontainers that can perform multiple functions. In this review, we delve into the progress made in the field of micro/nanocontainers-based intelligent coatings [12]. We examine various types of containers, their synthesis and encapsulation techniques, and provide specific examples. The review also explores different stimulus-responsive coatings and the models governing the release of encapsulated payloads. Finally, we discuss the application of these micro/nanocontainers across various fields, offering an in-depth analysis and presenting prospects. This comprehensive overview highlights the innovative strides being made in corrosion protection technology, aiming to enhance the longevity and effectiveness of protective coatings in a variety of challenging environments (Figure 1).
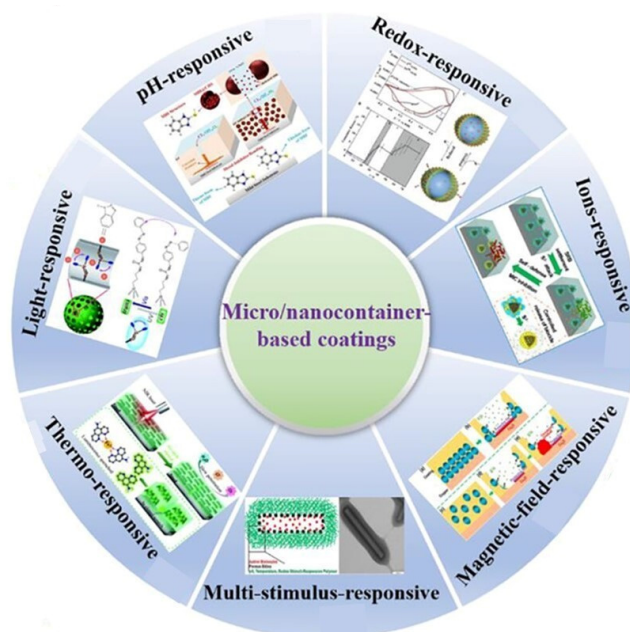
Figure 1. Illustrates various stimulus-responsive micro/nanocontainer coatings and their uses across fields, illustrating how they adapt to environmental changes like temperature or pH for applications in medicine, materials science, and environmental protection.

1.1. Advantages of Smart Self-Healing Coatings

The introduction of smart self-healing coatings represents a significant advancement in corrosion protection technologies. These coatings, which can be intrinsic or extrinsic, offer autonomous repair capabilities that are not found in traditional coatings. Intrinsic coatings, which utilize reversible bonds, can heal themselves without any external intervention, providing a continuous repair mechanism that can significantly extend the lifespan of metal surfaces. On the other hand, extrinsic coatings rely on micro/nanocontainers filled with healing agents that are released in response to environmental triggers, such as the presence of moisture or a change in pH, to repair damage. This targeted release ensures that healing agents are only used when necessary, reducing waste and potentially lowering long-term maintenance costs. The development of stimuli-responsive self-healing coatings, particularly through advancements in micro/nanocontainer technology, enhances the sensitivity and functionality of these coatings. This allows for the creation of coatings that can respond to multiple stimuli, further improving their effectiveness. Additionally, the incorporation of multifunctional properties such as self-reporting and anti-microbial actions not only contributes to corrosion protection but also adds value by monitoring the health of the coating and preventing microbial-induced corrosion.

1.2. Research Gaps and Disadvantages and Their Challenges

Despite the promising advantages, there are several challenges and disadvantages associated with smart self-healing coatings that need to be addressed. One of the primary limitations is the complexity involved in synthesizing and encapsulating the micro/nanocontainers, which can be a costly and time-consuming process. This complexity also extends to the design of multistimulus-responsive systems, which require precise control over the material properties to ensure effective functionality. Another challenge is the scalability of these technologies; producing these advanced coatings on an industrial scale can be difficult, limiting their widespread application. The volume of healing agent that can be encapsulated within micro/nanocontainers is another critical factor that dictates the efficacy of the repair. There is a limit to how much agent can be stored and released, which may not be sufficient for repairing larger cracks or damage. Furthermore, while the addition of multifunctional traits increases the coatings' applicability, it also adds to the

complexity and cost of the coating systems. These factors contribute to the current gap between laboratory-scale success and industrial-scale application, necessitating further research and development to overcome these hurdles and fully realize the potential of smart self-healing coatings in corrosion protection.

2. Exploring the World of Micro/Nanocontainers: Key to Advanced Extrinsic Self-Healing Coatings

Extrinsic self-healing coatings rely heavily on the integration of micro/nanocontainers, which play a crucial role in housing and dispensing active agents such as corrosion inhibitors and healing agents (Figure 2). These containers are designed with a capacity that ensures an adequate supply of these agents. When cracks form in the coating, the containers rupture, releasing their contents into the cracks through capillary action. This release allows the healing agents to interact with catalysts present in the coating, triggering a polymerization process that restores the coating's barrier properties. In terms of size, micro-scale containers typically range from 50 to 200 μm [13]. This size is optimal for two reasons: it facilitates the easy rupture of the containers under mechanical stress, and it provides adequate space to store enough healing agents. Nanocontainers, on the other hand, are more apt for carrying corrosion inhibitors due to their smaller size. These containers, whether through their inherent properties or surface modifications, are designed to respond to external environmental stimuli. This responsiveness enables the intelligent, timely release of the agents contained within, a process that underpins the active corrosion protection and self-healing performance of these advanced coatings [14].
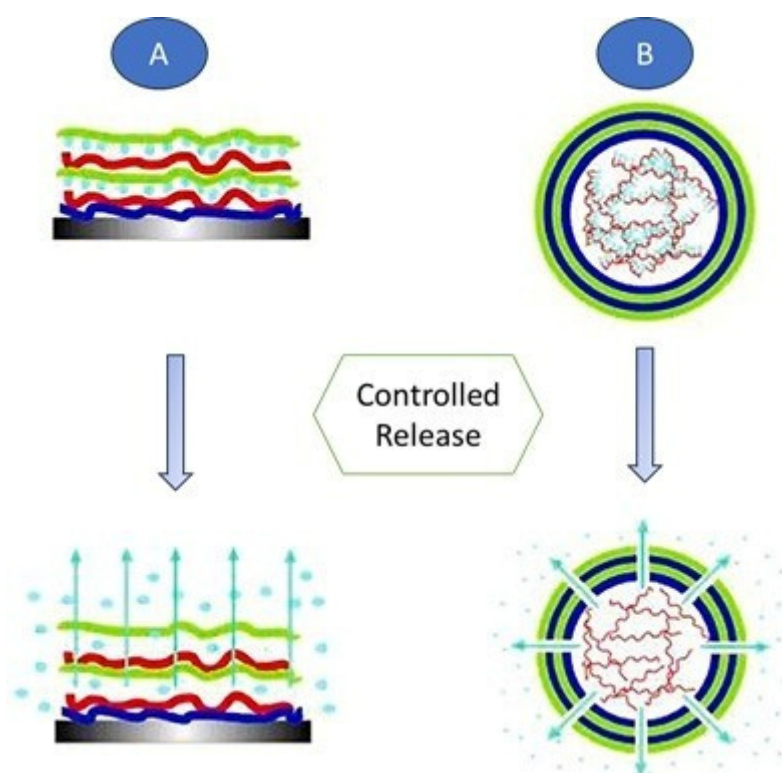
Figure 2. The diagram details two ways active agents are incorporated into coatings: (**A**) embedded directly in the coating for uniform functionality and (**B**) enclosed in micro/nanocontainers for protection until released by stimuli like temperature or pH changes. This smart encapsulation allows for precise agent release, enabling applications in drug delivery, corrosion prevention, and self-healing materials.

An added benefit of using micro/nanocontainers is their ability to prevent direct contact between the inhibitors and the coating matrix [11]. This separation is crucial for

maintaining the integrity of the coating and ensuring long-term corrosion resistance [6]. Depending on the materials and preparation processes used, these micro/nanocontainers can be broadly classified into three categories: organic, inorganic, and organic/inorganic hybrid [15]. In the realm of organic micro/nanocontainers, the focus is on using polymers and other organic compounds to create containers that are biocompatible and environmentally friendly [16]. Inorganic containers, on the other hand, often utilize materials like silica or metal oxides, known for their robustness and stability (Figure 3).
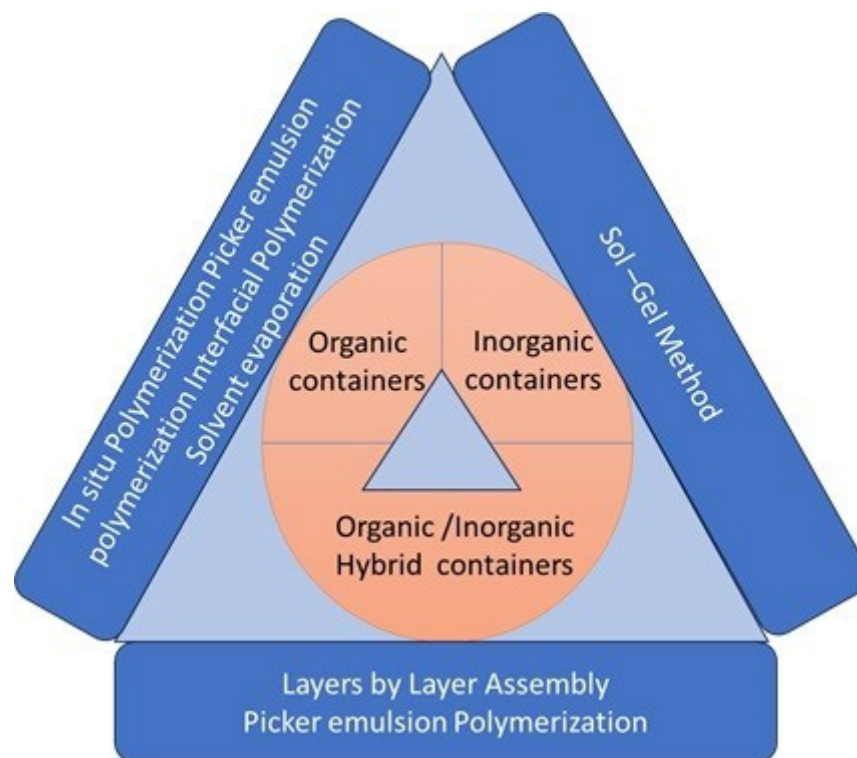
Figure 3. The figure categorizes various synthesis techniques for micro- and nanocontainers, crucial in nanotechnology and materials science for precision and control. Techniques range from self-assembly to complex methods like layer-by-layer assembly, sol–gel processing, and nano-precipitation, each chosen for specific advantages like size, permeability, and environmental responsiveness. The comparison highlights the best strategies for different applications, such as biomedical or industrial, guiding researchers and engineers in selecting the appropriate method.

Hybrid containers combine the best of both worlds, leveraging the advantages of organic and inorganic materials to create containers with enhanced properties [17]. The synthesis methods for these micro/nanocontainers vary greatly depending on the desired characteristics and application [18]. Techniques can range from simple chemical reactions to more complex processes like layer-by-layer assembly or self-assembly methods [19]. Each method has its unique advantages and limitations, influencing the final properties of the containers such as size, shape, permeability, and responsiveness to stimuli [14,18]. In this section, we delve deeply into the synthesis techniques of these diverse types of micro/nanocontainers. By exploring the methods used to create these tiny yet powerful components of self-healing coatings, we can gain a better understanding of their potential applications and how they are revolutionizing the field of corrosion protection [20]. The detailed discussion of these synthesis methods not only sheds light on the current state of the art but also paves the way for future advancements in the design and application of smart, responsive coatings [21].

The advantages of utilizing micro/nanocontainers in extrinsic self-healing coatings are significant, presenting a transformative approach in corrosion protection technologies.

These containers excel in precisely housing and dispensing healing agents, such as corrosion inhibitors, directly into the cracks formed in the coating. This targeted release mechanism, driven by capillary action and environmental stimuli, ensures an efficient and responsive healing process. The use of microcontainers, which are optimal in size, allows for the storage of ample healing agents and ensures their rupture under mechanical stress to initiate the healing process. On the other hand, nanocontainers are particularly suitable for carrying corrosion inhibitors due to their smaller size, enhancing the coatings' protective capabilities. The separation provided by these containers between the inhibitors and the coating matrix is crucial for maintaining the coating's integrity and ensuring its long-term corrosion resistance. The diversity in container materials—ranging from organic, to inorganic, to hybrid—offers a wide array of properties, including biocompatibility, robustness, and environmental friendliness, further broadening the applicability of these advanced coatings in various industrial sectors.

However, the methodology also presents certain disadvantages when compared to existing literature and technologies. The complexity and cost of synthesizing micro/nanocontainers can be significant, potentially limiting their widespread application. The precise control over the size, shape, and permeability of these containers, crucial for their optimal performance, requires advanced and sometimes costly fabrication techniques. Additionally, the long-term stability and environmental impact of these containers, especially those made from non-biodegradable materials, remain concerns that need further investigation. The interaction between the encapsulated agents and the polymer matrix during the healing process, as well as the potential for incomplete healing or release of agents, are challenges that necessitate ongoing research to fully understand and mitigate. Despite these drawbacks, the innovative approach of micro/nanocontainers in self-healing coatings represents a promising direction in corrosion protection technology, warranting further development and optimization to overcome these limitations.

2.1. Organic Micro/Nanocontainers: A Vital Component in Self-Healing Materials

Organic micro/nanocontainers stand out as one of the most promising components in the realm of self-healing materials [22]. These structures, which include forms like microcapsules, hollow fibers, and micro-network structures, offer a range of beneficial properties [11]. Their high load capacity allows for substantial storage of active healing agents. They also provide efficient protection against environmental degradation and boast high compatibility with various polymer matrices. One of the key advantages of organic micro/nanocontainers is their polymer shell, which offers robust protection for the encapsulated substances. This shell safeguards the contents from harsh environmental conditions, including extreme pH levels, temperature fluctuations, and exposure to light. As a result, these containers significantly extend the service life of self-healing materials in corrosive environments [23]. However, the process of creating these organic micro/nanocontainers is complex and multifaceted. It involves several stages, such as the polymerization reaction to form the container, encapsulation of the active agent, and the removal of by-products and solvents [11]. Despite these challenges, the unique benefits they offer make them an indispensable part of self-healing coatings.

Among the most common methods for preparing organic micro/nanocontainers is in situ polymerization [24]. This process involves polymerizing the monomers directly around the active agent, forming a protective shell. This method is favored for its ability to create a uniform and consistent shell, which is crucial for effective encapsulation and controlled release of the active agent. Another popular technique is the use of Pickering emulsion [25]. This method utilizes solid particles to stabilize the emulsion droplets, which are then used as templates for the formation of micro/nanocontainers [26]. Pickering emulsion is particularly useful for creating containers with specific shapes and sizes, allowing for precise control over the encapsulation process [26]. These preparation methods, along with others in the field, highlight the sophistication and innovation driving the development of organic micro/nanocontainers. Each method has its specific advantages and challenges,

but all contribute to the overall effectiveness and efficiency of self-healing materials. As research in this area continues to evolve, we can expect further advancements that will enhance the performance and application of these vital components in corrosion protection and beyond [27].

Organic micro/nanocontainers, with their diverse preparation methods, offer a wide range of possibilities for self-healing materials. Beyond in situ polymerization and Pickering emulsion polymerization, other notable methods include interfacial polymerization and solvent evaporation, each with unique advantages and applications [28]. Interfacial polymerization is particularly well suited for large-scale production of organic capsules. This method involves a reaction at the interface between two incompatible solutions, each containing different monomers for the shell and core [29]. Capsules with the encapsulated agent at the core are formed at this interface. Sun's work with hex methylene diisocyanate in double-layered microcapsules is a prime example. The inner polyurea shell layer, created by interfacial polymerization, resulted in microcapsules with precise dimensions and high encapsulation efficiency [30]. This method is known for its mild reaction conditions and the ability to control the size of the capsules, although the selection of pre-monomers and synthesis parameters is crucial for optimal performance [11].

In a recent development, Chen [31] innovated in the field of smart materials by modifying poly-N-isopropylacrylamide particles, integrating them with Nile Red, a fluorescent dye. These modified particles were then utilized as a Pickering emulsifier, a type of stabilizer for emulsions. The oil phase of this emulsion was uniquely composed of pH-sensitive monomers and an oil-soluble fluorescent green dye. The resultant microcapsules showcased a dual-layered structure: an outer shell made of the temperature-sensitive poly-N-isopropylacrylamide@Nile Red and an inner core containing the oil-soluble fluorescent green substance (Figure 4). This innovative design allows for the selective release of the encapsulated materials—Nile Red and the oil-soluble fluorescent green—in response to different external stimuli. The ability to respond to various environmental changes, such as temperature fluctuations or pH variations, is a critical feature of these microcapsules. The presence of Nile Red in the shell offers a distinct advantage, as it enables the visualization of the microcapsules and their behavior under different conditions. The implications of Chen's research are significant, particularly in the development of smart self-healing materials. These multicompartmental microcapsules, with their diverse stimulus-responsive capabilities, hold immense potential for applications where controlled release and reaction to environmental changes are crucial [31,32]. For instance, in self-healing materials, these microcapsules can respond to damage or environmental changes by releasing their contents to repair or modify the material, thereby enhancing its durability and functionality [31]. Chen's work marks a notable advancement in the field of smart materials, paving the way for more innovative applications and technologies.

The solvent evaporation technique is another common method for creating organic capsules. It involves dissolving both the polymer shell and core materials in an organic solvent, followed by the gradual addition of a stabilizer. This process forms polymer droplets containing the core materials, which solidify upon solvent evaporation, resulting in microcapsules. Gu's synthesis of bisphenol A cyanate ester/polyglycidyl methyacrylate microcapsules demonstrates this technique's effectiveness in producing capsules with specific shapes and sizes [11] Thus the prepared microcapsules were oval in shape with an average diameter of 31.5 μm and a wall thickness of 2.2 μm (Figure 5). This method allows for fine control over the properties of the microcapsules by adjusting experimental parameters, and it is particularly suitable for solid core materials due to its high encapsulation efficiency and low solvent residue. An emerging and intriguing addition to organic containers is the 2D covalent organic framework (COF) [33]. COFs are attracting attention for self-healing materials design due to their flexible, porous structure, specific surface area, and controllable pore size. Formed by covalent bonding of organic elements, their porous structure not only facilitates material permeation but also serves as a carrier for corrosion inhibitors. This unique capability positions COFs as an innovative solution for

active corrosion protection of metal substrates [33]. Their weak interlayer interactions and customizable properties make them a promising candidate for future advancements in self-healing material technologies [34]. In summary, the development and synthesis of organic micro/nanocontainers are pivotal in advancing self-healing materials. Each method—be it in situ polymerization, Pickering emulsion polymerization, interfacial polymerization, or solvent evaporation—brings distinct advantages and possibilities. These techniques, coupled with the introduction of innovative materials like COFs, are pushing the boundaries of what is achievable in the realm of corrosion protection and self-repairing systems [33,34]. As research in this area continues to evolve, we can anticipate more sophisticated and efficient self-healing materials that cater to a wide range of industrial applications.
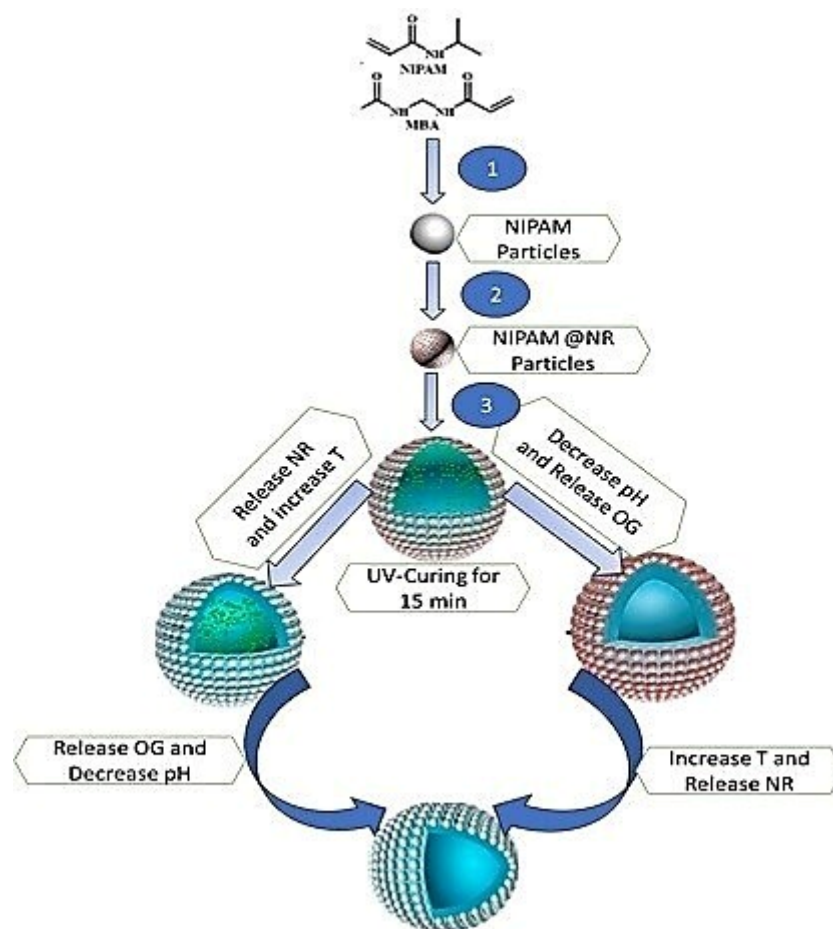
Figure 4. Shows the creation of dual-stimuli-responsive microcapsules with multiple compartments. Starting with poly-N-isopropylacrylamide particles known for their temperature sensitivity, these are then combined with Nile Red, a fluorescent marker, to monitor encapsulation and release. The mixture is used as a Pickering emulsifier for a stable emulsion, forming the basis of the microcapsules. This enables them to react to both temperature changes and chemical triggers, allowing for precise content release, crucial for targeted drug delivery and smart materials. Reprinted/adapted with permission from Ref. [31]. 2020, ACS Publications.

The field of organic micro/nanocontainers has seen remarkable advancements, particularly with the introduction of covalent organic frameworks (COFs) that offer enhanced compatibility and dispersion in organic matrices. Liu's synthesis of TpPa-1 COF nanocontainers, which involved a Schiff base reaction, is a noteworthy example. These containers were used to encapsulate benzotriazole (BTA) inhibitors, and when embedded into epoxy coatings, they significantly improved corrosion resistance [33]. The BTA/TpPa-1 embedded epoxy coatings demonstrated exceptional durability with an impedance value of $6.45 \times 10^8 \ \Omega \ cm^2$

after 60 days. This research also explored the hybridization of COF-modified graphene oxide (GO) sheets as nanofillers, further enhancing the corrosion resistance of epoxy coatings. The size of organic containers, which can range from 1 to 1000 μm, is largely influenced by synthesis parameters such as emulsifier content, agitation speed, and reaction time [35]. Generally, increasing the emulsifier content or agitation speed results in smaller-sized containers with a narrower size distribution. However, the diameter of these containers is not just a matter of fabrication precision; it also has a significant impact on their mechanical properties. Smaller containers often withstand higher loads compared to larger ones, but they must balance robustness with the ability to rupture under the right conditions to release their healing agents effectively [35,36].
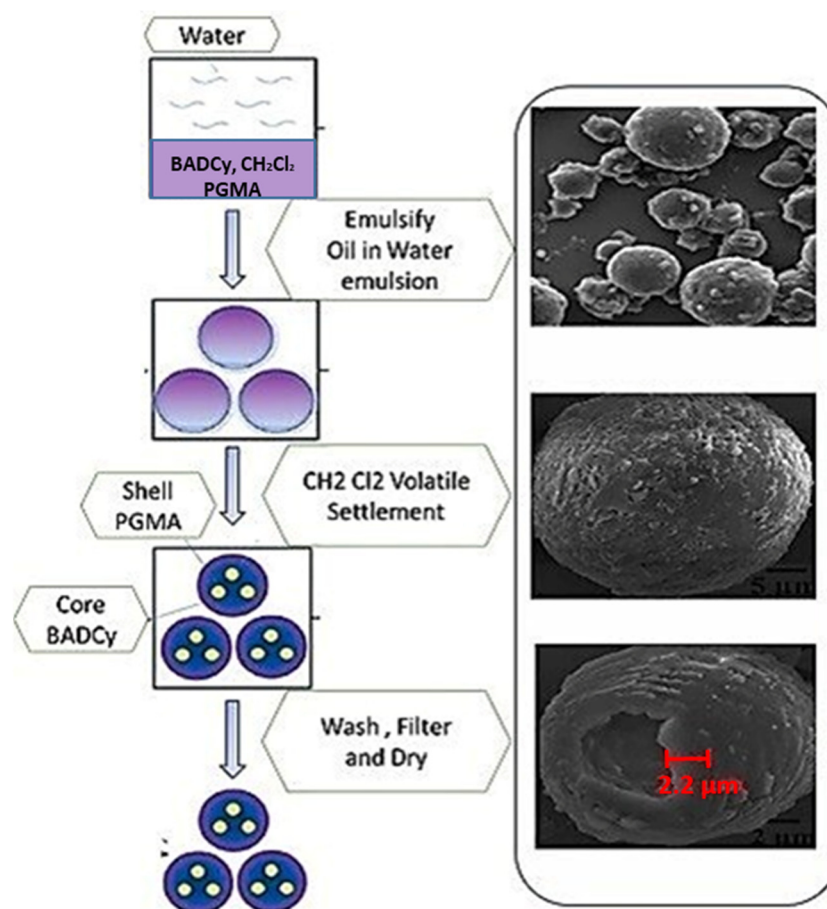
Figure 5. Illustrates the synthesis of microcapsules from bisphenol. A cyanate ester and polyglycidyl methyacrylate using solvent evaporation. This process involves dissolving polymers in a volatile solvent, creating an emulsion, and then evaporating the solvent to form a polymer shell that encapsulates active agents. The figure highlights the capsules' morphology, showcasing spherical shapes with varying surface textures. The combination of materials provides thermal stability, mechanical strength, and chemical resistance, making these microcapsules ideal for high-temperature industrial applications like controlled-release coatings. The figure explains the synthesis process and the characteristics of the microcapsules, emphasizing the factors that determine their structure and properties.

An important consideration in the development of micro/nanocontainers is ensuring that they possess the appropriate mechanical strength and size. If the outer shell is too robust, the containers might not rupture as required for the repair effect. Conversely, if they are too weak, they may not withstand the conditions within the coating matrix. Achieving this balance is crucial for the optimal performance of smart self-healing coatings. In conclusion, the synthesis and application of organic micro/nanocontainers are key to advancing self-healing materials technology [7,12,16]. The diversity of synthesis methods

and materials, including innovative approaches like COFs and GO sheet hybrids, offers a wide range of possibilities for enhancing the durability and effectiveness of protective coatings [7]. The careful selection of container size, material, and mechanical properties is essential to realizing the full potential of these advanced materials in various industrial applications. As the field continues to evolve, we can expect further innovations that will push the boundaries of self-healing technology and corrosion protection [20,24].

The advantages of organic micro/nanocontainers have revolutionized the field of self-healing materials by offering high load capacity for active healing agents, which significantly enhances the efficiency of corrosion protection and material repair. Their compatibility with various polymer matrices and the ability to protect encapsulated substances from harsh environmental conditions stand out as critical benefits. This compatibility ensures that the healing agents remain potent and ready to act upon the occurrence of damage. The innovation in the synthesis and application of these containers, including methods like in situ polymerization and Pickering emulsion, contributes to the precise control over encapsulation, enabling a consistent and effective healing response. Furthermore, the development of covalent organic frameworks (COFs) as a new class of micro/nanocontainers has opened up possibilities for enhanced dispersion and compatibility within organic matrices, further broadening the scope and efficiency of self-healing materials.

Despite these advancements, the complexity of creating organic micro/nanocontainers poses significant challenges. The multifaceted process involving polymerization, encapsulation of the active agent, and the subsequent removal of by-products and solvents can be resource-intensive and technically demanding. This complexity may limit the scalability and cost-effectiveness of producing these self-healing materials for broader industrial applications. Additionally, achieving the optimal balance between the mechanical strength and the responsive rupture of the containers remains a critical challenge. Containers that are too robust may fail to release their healing agents when needed, while those too fragile may rupture prematurely or fail to withstand the operational environment, thus compromising the healing efficacy.

In comparison to the existing literature, these methodologies underscore a significant leap in the targeted delivery and controlled release of healing agents, offering a more responsive and efficient approach to corrosion protection and material repair. However, the challenges highlight the need for ongoing research to refine synthesis techniques, improve cost-efficiency, and ensure the practical applicability of these advanced materials in real-world conditions. The continuous evolution of synthesis methods and the exploration of new materials like COFs and graphene oxide (GO) sheet hybrids for containers suggest a promising trajectory for overcoming these hurdles, pushing the boundaries of self-healing technology toward more sophisticated and widely applicable solutions.

2.2. Inorganic Micro/Nanocontainers: Focusing on Their Structure, Applications, and Limitations

Inorganic micro/nanocontainers are characterized by their small, cavity-like structures capable of holding active agents within nanoparticles [37,38]. These containers undergo surface modification for enhanced compatibility and controlled release of these agents. They are designed to respond to external microenvironments, leading to reversible or irreversible structural changes, which help in releasing functional species like corrosion inhibitors into targeted areas. These inorganic containers are small and stable and offer broad coverage and an easy encapsulation process. Compared to organic counterparts, inorganic containers simplify the inhibitor encapsulation process and enhance the thermomechanical properties and barrier performance of self-healing systems [16,38]. Commonly used inorganic containers include titanium dioxide, cerium dioxide, mesoporous silica, nano-clays, and others. They can encapsulate both inorganic (like cerium salt) and organic inhibitors.

However, there are significant drawbacks. One major issue is their poor compatibility with polymer materials, leading to aggregation and potentially causing micro defects that accelerate damage. Additionally, their capacity to hold active agents is relatively low (usually less than 20%), limiting their effectiveness in long-term corrosion protection. The main manufacturing method for these containers is the sol–gel process, which is conducted

at room temperature and involves high chemically active components like tetraethoxysilane. This method, while mild, can result in containers that are not compact and have limited capacity for active agents. The Stober method, developed for controlling the growth of silica particles, offers some improvements but still presents challenges in terms of time efficiency and load capacity [39]. In summary, inorganic micro/nanocontainers show promise in applications like corrosion inhibition due to their unique properties, such as ease of encapsulation and enhancement of self-healing systems. However, challenges in compatibility with polymers, limited active agent capacity, and manufacturing complexities need addressing to fully realize their potential [40].

The specifics of tetraethoxysilane-based inorganic micro/nanocontainers, their synthesis, applications, and comparative attributes, are as follows. Tetraethoxysilane is used under alkaline conditions to produce particles ranging from less than 0.05 μm to 2 μm in diameter. This method has led to the creation of various inorganic hollow spheres as micro/nanocontainers [41]. A notable example is the work of Wang, who utilized the sol–gel method to create hollow mesoporous zirconia nanospheres. These nanospheres were loaded with L-carnosine, a green corrosion inhibitor [42]. The release of L-carnosine from these containers is pH-sensitive, with 90% being released in just 70 min in a pH 10.0 environment. These nanospheres were then incorporated into water-based epoxy resin coatings to develop an intelligent anti-corrosion system [11]. Studies using the scanning vibrating electrode technique revealed that coatings containing these nanocontainers showed significantly lower anodic current densities compared to pure epoxy coatings, indicating better corrosion resistance [43].

In comparison to organic micro/nanocontainers, inorganic containers generally maintain constant shapes and exhibit stable physicochemical and mechanical properties. However, they also tend to have low compatibility with organic coatings and often lack responsive functionality. Furthermore, the mechanisms behind the release of encapsulated agents differ between inorganic and organic containers [44]. For organic containers, release is typically driven by chemical reactions at the shell wall, such as covalent bond breakage or depolymerization. In contrast, inorganic containers rely more on physical or mechanical effects like external pressure, thermomechanical destruction, or the porosity of the container surface [45]. In summary, while inorganic micro/nanocontainers made from materials like tetraethoxysilane offer advantages in stability and shape retention, they face challenges in compatibility with organic coatings and lack certain responsive functionalities. Their release mechanisms are primarily physical, contrasting with the chemical-based release in organic containers. Despite these differences, their application in areas like corrosion protection, as illustrated by the L-carnosine loaded zirconia nanospheres, demonstrates their potential in advanced material technologies.

Inorganic micro/nanocontainers offer a significant leap forward in the development of self-healing materials, particularly in the context of corrosion protection. These containers distinguish themselves through their stable, small, cavity-like structures capable of encapsulating and subsequently releasing active agents like corrosion inhibitors in response to specific environmental triggers. This innovative approach facilitates the enhancement of thermomechanical properties and barrier performance of coatings, addressing the critical need for durable and efficient corrosion protection systems. The primary benefits of utilizing inorganic micro/nanocontainers include their enhanced stability and ability to undergo surface modification, which ensures compatibility and controlled release of active agents. This feature is pivotal in applications requiring precise targeting and release of functional species to mitigate corrosion effectively. Inorganic containers like titanium dioxide and mesoporous silica simplify the encapsulation process and are inherently more stable, offering broad coverage and an easy encapsulation process. Their design for responding to external microenvironments leads to structural changes that help in the efficient release of functional species into targeted areas, thus significantly improving the self-healing capabilities of materials.

Several challenges accompany the use of inorganic micro/nanocontainers. One of the most notable drawbacks is their relatively poor compatibility with polymer materials,

which can lead to aggregation and the formation of micro defects within the coating matrix, potentially accelerating damage. Furthermore, the capacity of these containers to hold active agents is generally limited (usually less than 20%), which might constrain their effectiveness in providing long-term corrosion protection. Additionally, the manufacturing process, predominantly the sol–gel method, while mild and conducted at room temperature, may result in containers with limited compactness and reduced capacity for active agents. When compared to organic micro/nanocontainers, inorganic variants offer a contrasting profile of advantages and limitations. Organic containers are praised for their high compatibility with various polymer matrices and efficient protection against environmental degradation, whereas inorganic containers excel in stability and ease of encapsulation but struggle with compatibility issues and limited active agent capacity. Despite these challenges, the unique properties of inorganic micro/nanocontainers, such as their ability to enhance the thermomechanical properties and barrier performance of self-healing systems, underscore their potential in advancing the field of corrosion protection and beyond. Addressing the limitations related to compatibility, agent capacity, and manufacturing complexities remains a critical area of focus for future research to fully leverage the advantages offered by inorganic micro/nanocontainers in self-healing materials.

2.3. Micro/Nanocontainers: Their Composition, Manufacturing Methods, and Applications

Organic/inorganic hybrid micro/nanocontainers are characterized by a hollow core and a hybrid wall composed of both inorganic and organic materials. These containers combine the advantages of organic micro/nanocontainers (multifunctionality and adjustable properties) with the strengths of inorganic micro/nanocontainers (good physiochemical stability and strong mechanical properties) [46]. However, the rigid and inert nature of inorganic containers often limits their application. Several types of hybrid micro/nanocontainers are mentioned, including inorganic nanoparticles with layer-by-layer polyelectrolytes, polymer-coated inorganic nanospheres/nanotubes, inorganic-coated organic hollow nanospheres, and metal–organic frameworks (MOFs) [47]. The layer-by-layer (LBL) assembly technique is highlighted for its ability to create tightly arranged molecular structures. This technique has been used to produce thin films and hybrid capsules with controlled thickness, composition, and organization. An example of the LBL technique is Caruso's fabrication of silica-polymer hybrid capsules, incorporating various nanoparticles like Fe_3O_4 and graphene oxide [48]. These hybrid containers offer stable structures and multifunctionality, expanding their application range. The permeability of these containers can be controlled by adjusting environmental factors like pH and temperature, making them responsive to multiple stimuli. In the field of corrosion protection, LBL-assembled micro/nanocontainers have been used for pH-triggered release of inhibitors [49]. These containers have also found applications in storage, wastewater remediation, and drug delivery. Furthermore, functional inorganic substances can be deposited onto polymer capsules to create multifunctional organic/inorganic hybrids. Examples include graphene oxide microcapsules and silica/polyurea hybrid microcapsules with impressive self-healing and corrosion resistance properties [49].

MOFs are another example of organic/inorganic hybrid containers, known for their high surface area, stability, and adjustable morphology. They have been used in a variety of fields, including energy storage and drug delivery [50]. The paragraph mentions a specific MOF, ZIF-8, which is pH-responsive and suitable for encapsulating active agents. Overall, organic/inorganic hybrid micro/nanocontainers combine the best features of organic and inorganic containers, offering excellent physicochemical properties and multiresponsive functionalities [51]. They are compatible with various coating matrices and are critical in developing efficient self-healing technologies. However, their performance is influenced by the organic components in the hybrids, and their dispersion within the coating is crucial for optimal function. A table in [52] provides examples of different types of stimulus-responsive micro/nanocontainers.

The process of releasing substances from micro- and nanocontainers is a multifaceted and intricate procedure, primarily due to the various complex physicochemical reactions involved. Accurately modeling this release process is challenging, requiring the consideration of multiple steps. To address this complexity, several mathematical models are employed, with the Higuchi, zero-order, and Korsmeyer–Peppas models being the most prominent [53]. These models are selected based on their suitability under specific conditions, with the Korsmeyer–Peppas model playing a pivotal role in determining the applicability of the Higuchi and zero-order models [54]. When it comes to choosing the most fitting model to study release kinetics, the coefficient of determination (R^2) is commonly used to gauge a model's accuracy. However, this method has its limitations, as R^2 values can increase with the addition of more parameters, which may not always be relevant. To overcome this, the adjusted correlation coefficient (R^2 adjusted) is recommended. This coefficient adjusts for the number of data points and model parameters, offering a more precise measure of a model's relevance to the actual release conditions. These kinetic models are invaluable in shedding light on the diffusion dynamics of the encapsulated inhibitors and the degradation of the coating matrix. Such insights are crucial for exploring and understanding the mechanisms behind corrosion protection in smart anti-corrosive coatings. This knowledge is instrumental in enhancing existing corrosion protection strategies and in the development of new, more efficient systems with finely tuned release mechanisms (Table 1).

The methodology involving organic/inorganic hybrid micro/nanocontainers represents a significant advancement in the development of self-healing materials, blending the multi-functionality and adjustable properties of organic containers with the physicochemical stability and mechanical robustness of inorganic ones. This hybrid approach allows for the creation of containers that offer both stability and flexibility, a combination that is particularly valuable in applications requiring controlled release mechanisms under specific conditions, such as in corrosion protection, drug delivery, and environmental remediation. One of the key strengths of these hybrid micro/nanocontainers lies in their versatile functionality, which can be fine-tuned through the layer-by-layer (LBL) assembly technique. This method enables precise control over the thickness, composition, and molecular organization of the containers, allowing for the incorporation of various nanoparticles to achieve desired properties. For instance, the integration of Fe_3O^4 and graphene oxide into silica-polymer hybrid capsules enhances their structural stability and expands their application range. Moreover, these containers' responsiveness to environmental stimuli such as pH and temperature changes enables the smart release of encapsulated agents, making them highly effective in self-healing applications where such controlled release is crucial.

Table 1. Presents an overview of micro- and nano-sized containers responsive to specific stimuli like temperature, pH, light, magnetic fields, or chemicals. These containers release contents like drugs or dyes in a targeted manner, useful in medical drug delivery and smart coatings. The table categorizes them by response mechanism, composition, size, and applications, offering insights into their properties and practical uses.

SNo	Trigger Factor	Type	Micro/Nanocontainers	Inhibitors/Healing Agent	Reference
1	pH	Organic/inorganic hybrid micro/nanocontainers	ZIF	Benzimidazole	[55]
	pH		MOF/graphene oxide	2-Mercaptobenzimidazole (MBI)	[56]
	pH		SiO$_2$/polyelectrolyte layers	BTA	[56]
	Thermo		Silica-poly(N-isopropylacrylamide)	rhodamine B	[57]

Table 1. *Cont.*

SNo	Trigger Factor	Type	Micro/Nanocontainers	Inhibitors/Healing Agent	Reference
2	pH	Inorganic micro/nanocontainers	LDH	sodium molybdate	[58]
	pH		Graphene	BTA	[59]
	Redox		$Fe_3O_4@mSiO_2$	8-HQ	[60]
	pH/redox		Mesoporous SiO_2	2-mercaptobenzothiazole (MBT)	[61]
	NIR		TiN@mesoporous SiO_2	BTA	[62]
	NIR/UV		TiO_2/carbon black nanoparticles	fluorine silane	[62]
3	Mechanical/pH		Poly(urea-ormaldehyde)	BTA	[63]
	UV		Poly(urea-urethane)	2-oxoacetates	[64]
	Chloride ions		Alginate hydrogel capsules	silver	[65]
	Thermo		Calcium alginate gel capsules	Imidazoline quaternary ammonium salt	[66]
	Redox		Polyaniline/poly(2,5-dimercapto-1,3,4-thiadiazole)	2,5-dimercapto-1,3,4-thiadiazole	[67]

The development of organic/inorganic hybrid containers is not without its challenges. The integration of inorganic components can sometimes result in poor compatibility with polymer matrices, leading to potential aggregation issues. Moreover, the complexity of creating these hybrid containers, which involves sophisticated synthesis techniques like the LBL assembly, may pose scalability and cost-effectiveness concerns. Additionally, the performance of these containers heavily relies on the organic components' behavior within the hybrid, requiring careful consideration of dispersion within the coating to ensure optimal functionality. Compared to the existing literature, the proposed methodology of utilizing organic/inorganic hybrid micro/nanocontainers introduces a novel approach that leverages the synergistic effects of combining organic and inorganic materials. This results in containers with enhanced mechanical properties, chemical resistance, and multifunctionality over purely organic or inorganic containers. However, addressing the aforementioned compatibility and manufacturing challenges is essential for fully realizing the potential of these advanced materials in practical applications. As research in this field progresses, further innovations and refinements in synthesis techniques and material selection are expected to overcome current limitations, paving the way for broader industrial adoption of these sophisticated self-healing systems.

3. Exploring the Dynamic Release Patterns of Encapsulated Agents from Micro and Nanocontainers

The encapsulation process of active agents in micro/nanocontainers is a critical aspect in the field of material science, particularly in the development of protective coatings to combat corrosion. This process involves the containment of corrosion inhibitors within these tiny carriers through physical or chemical interactions. The fundamental idea is that when the coating is exposed to certain external stimuli, it triggers the micro/nanocontainers to release these inhibitors directly at the sites of corrosion, effectively halting or slowing down the corrosion process. However, several factors significantly influence this encapsulation and release process. These include the capacity of the containers to hold the inhibitors (loading capability), how well the particles are distributed (dispersion status), the size of the particles (particle size), how well the inhibitors dissolve in the coating (solubility), and the type of corrosion inhibitors used. These factors collectively affect the rate and efficiency at which the inhibitors are released, known as release kinetics. Understanding and optimizing these release kinetics is essential for ensuring that the inhibitors are released effectively and at the right time to prevent corrosion [68].

In the realm of controlled release kinetics, several models are employed to predict and understand the release behavior of encapsulated substances. The zero-order model proposes a constant release rate, ideal for scenarios requiring steady and predictable inhibitor release. The first-order model, in contrast, is used when the release rate diminishes over time, particularly as the remaining quantity of the inhibitor decreases. The Higuchi model, grounded in Fick's law, correlates the release rate with the square root of time and is frequently applied to modified release dosage forms [69]. The Hixson–Crowell model takes into account the erosion of the matrix containing the inhibitors, positing that the release is governed by this erosion. For situations where the release mechanism is complex or ambiguous, the Korsmeyer–Peppas model is utilized, capable of describing various release phenomena in polymeric systems [70]. Lastly, the Hopfenberg model centers on the matrix's erosion as the primary rate-limiting step, suggesting that diffusion resistance is a negligible factor in the erosion process. Each of these models offers a unique perspective on the kinetics of release, catering to different scenarios and types of encapsulated substances. Real-world applications of these models can be seen in various studies. For example, Cao's research on 2-mercaptobenzothiazole in polyaniline microspheres showed the utility of these models in predicting the release behavior in a saline solution. Similarly, studies by Adsul [71] and Ghodke [72] on halloysite nanotubes further demonstrate the practical application of these models in understanding the kinetics of inhibitor release under various conditions. In summary, the encapsulation and controlled release of corrosion inhibitors in micro/nanocontainers is a sophisticated process influenced by multiple factors. The development and application of various kinetic models are crucial for predicting and optimizing this release, ensuring the effective prevention of corrosion in different environments.

Previous studies explored the release of fragrance molecules from nanocontainers; it was observed that the amount of fragrance released increased as the pH value rose from 3 to 7 [73]. To understand this release behavior, various release kinetic models were applied. Among these, the Korsmeyer–Peppas model demonstrated the best fit with an R^2 value of 0.9544, indicating that the release process was influenced by time and the initial concentrations of the substances [70]. However, accurately modeling the release process of encapsulated substances is often challenging due to the multiple steps involved, each characterized by different and complex physicochemical reactions. While models like the Higuchi, zero-order, and Korsmeyer–Peppas are commonly used and have shown significant applicability, each has specific conditions under which they are most effective. The Korsmeyer–Peppas model, in particular, is noted for its ability to act as a deciding factor between the Higuchi and zero-order models, representing two extreme cases in the release process. When selecting the most appropriate model to describe release kinetics from micro/nanocontainers, the R^2 value is typically used to assess the fit of a model. However, the R^2 value can be misleading as it tends to increase with the addition of more parameters, regardless of the relevance of these additional variables. To counter this, using the adjusted correlation coefficient (R^2 adjusted) is proposed, especially when comparing models with varying numbers of parameters [70]. This coefficient takes into account the number of data points (n) and the number of parameters in the model (p), providing a more accurate representation of the model's applicability. The integration of different kinetic models is crucial in understanding the diffusion processes and the degradation of the coating matrix in the release of encapsulated inhibitors from micro/nanocontainers. Such insights are invaluable in exploring the corrosion protection mechanisms of smart anticorrosive coatings. They aid in enhancing current corrosion protection systems and in developing new systems with more precise and controlled release behaviors [74].

The methodology surrounding the encapsulation and release of active agents from micro/nanocontainers is pivotal in the advancement of materials science, especially for creating protective coatings against corrosion. This process, which leverages both physical and chemical interactions for encapsulation, is designed to release corrosion inhibitors precisely when and where needed, upon exposure to specific external stimuli. This strategic release mechanism aims to halt or decelerate the corrosion process effectively. However,

the efficiency of this encapsulation and subsequent release is subject to various influencing factors such as the containers' loading capacity, dispersion within the coating, particle size, solubility of inhibitors, and the nature of the corrosion inhibitors themselves. These elements collectively dictate the release kinetics, which is crucial for the timely and effective deployment of inhibitors to combat corrosion.

The use of micro/nanocontainers for encapsulating active agents presents a sophisticated approach to corrosion protection, allowing for a controlled and targeted release of inhibitors. This methodology benefits from employing several kinetic models (e.g., zero-order, first-order, Higuchi, Hixson–Crowell, Korsmeyer–Peppas, and Hopfenberg models) to predict and understand the release behavior of encapsulated substances, catering to various scenarios and encapsulated substance types. Such models are instrumental in optimizing release kinetics, ensuring that inhibitors are effectively deployed to prevent corrosion.

Despite the apparent benefits, challenges remain in accurately predicting and optimizing the release kinetics due to the complexity of the encapsulation and release processes. These processes involve multiple steps, each characterized by different and intricate physicochemical reactions, making it difficult to model the release behavior accurately. Additionally, while kinetic models like the Korsmeyer–Peppas offer valuable insights into release phenomena, the reliance on R^2 values for model fit assessment can be misleading. This is because R^2 values tend to increase with the addition of more parameters, which may not always be relevant. To address this, the adjusted correlation coefficient (R^2 adjusted) is recommended for a more accurate representation of a model's applicability.

Compared to the existing literature, this methodology underscores the intricate balance required in designing micro/nanocontainers for corrosion protection. The dynamic release patterns of encapsulated agents from these containers need to be thoroughly understood and optimized for the effective prevention of corrosion. While the models provide a foundation for predicting release kinetics, ongoing research and development are crucial to refine these models further, enhance the precision of release mechanisms, and overcome the limitations identified in current methodologies. This evolution is essential for advancing the field of protective coatings and developing new systems with more precise and controlled release behaviors, ensuring robust corrosion protection in diverse environments.

4. Stimulus-Responsive Coatings Represent an Advancement in Material Science

Stimulus-responsive coatings are a class of smart materials capable of responding to changes in their environment under various external stimuli. These coatings adjust their physicochemical properties like shape, solubility, permeability, and surface wettability to adapt to corrosive environments, finding applications in drug delivery, tissue engineering, sensing, and notably in metal corrosion protection [75]. Traditional anti-corrosive coatings primarily act as physical barriers against corrosive ions. However, they are vulnerable to damage from these ions or mechanical actions, leading to the eventual corrosion of the metal substrate. In contrast, micro/nanocontainers-based stimulus-responsive coatings can swiftly and effectively respond to external stimuli such as pH, light, temperature, and ions [16]. This response triggers the release of encapsulated corrosion inhibitors, offering active corrosion protection by repairing damaged areas and preventing further corrosion.

4.1. pH-Responsive Coatings

The dispersion of these micro/nanocontainers within the polymer matrix is a critical factor influencing the coating's anti-corrosive performance. Issues such as compatibility and agglomeration can negatively impact the barrier properties of the polymer coatings. Furthermore, achieving precise control over the stimuli-responsive release behavior of the encapsulated substances is crucial for long-term corrosion resistance. Specifically, pH-responsive coatings are highly relevant in this context. Metal corrosion often leads to pH fluctuations, with decreases in pH at anodic regions and increases at cathodic areas. The pH-responsive micro/nanocontainers can detect these changes and react accordingly, releasing

corrosion inhibitors as needed [16]. These containers often use polyelectrolyte molecules as "gatekeepers", controlling the release of encapsulated agents and responding to pH changes. Researchers like Shchukin have employed techniques like layer-by-layer (LBL) self-assembly to create effective pH-responsive layers on nanocontainers (Figure 6) [76].
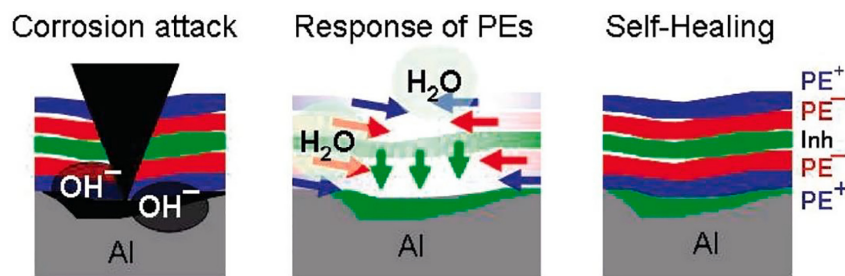
Figure 6. Shows a schematic of the self-healing process in a layer-by-layer (LBL) polyelectrolyte coating, designed for metal corrosion prevention. It details how localized pH changes from initial corrosion trigger the release of corrosion inhibitors (Inh) from layers of positively and negatively charged polyelectrolytes. These changes cause the polyelectrolytes to reconfigure, releasing inhibitors that neutralize corrosive agents and repair the coating, restoring metal surface integrity. The figure highlights the coating's dynamic response to corrosion, demonstrating its application in durable metal protection across industries. Reprinted/adapted with permission from Ref. [76]. 2015, RSC Publishing.

Various polyelectrolytes, such as polydopamine, chitosan, and polyacrylic acid, have been used in these applications. For example, Haddadi's synthesis of MBI@carbon hollow spheres illustrates the effectiveness of these coatings in providing corrosion resistance. However, challenges remain, including the range of triggering pH values, the difference in response for various metals in different environments, and the potential for uncontrolled release due to external pH changes. Moreover, the reversibility of the release mechanism often means that the coatings can only provide a temporary self-healing effect. In summary, while stimulus-responsive coatings, particularly pH-responsive types, offer significant advancements in metal corrosion protection, ongoing research and development are needed to address their limitations and enhance their effectiveness in diverse environmental conditions [16].

One prominent example of such coatings is pH-responsive coatings. Metal corrosion often involves fluctuations in local pH levels due to the dissolution and hydrolysis of metal ions in the anodic regions and the reduction reactions in cathodic areas. pH-responsive micro/nanocontainers can detect these pH changes and release encapsulated corrosion inhibitors accordingly. This intelligent response system involves materials like polyelectrolytes, which act as gatekeepers, regulating the release of the agents in response to pH variations. These materials can undergo protonation or deprotonation, or their solubility can change in response to pH, thereby triggering the release of the inhibitors. This mechanism provides a smart, targeted approach to corrosion protection. Despite these advancements, there are still challenges to be addressed in the development of pH-responsive coatings [76]. The range of pH values that trigger the coating's response, the differing behaviors of metals in various corrosive environments, and the potential for unintended release under fluctuating external pH conditions are significant concerns. Moreover, the reversible nature of the release mechanisms often means that the coatings can only offer a temporary solution to corrosion, requiring further research and refinement. In summary, stimulus-responsive coatings, particularly pH-responsive ones, represent a significant step forward in the field of corrosion protection [77]. While they offer promising solutions, ongoing research is essential to optimize their performance, address their limitations, and tailor them for a wider range of applications and environmental conditions.

Stimulus-responsive coatings, particularly those incorporating micro/nanocontainers, represent a significant leap forward in the realm of material science, offering a dynamic ap-

proach to combating metal corrosion compared to traditional anti-corrosive coatings. These smart materials can adapt their physicochemical properties in response to environmental changes, providing targeted corrosion protection through the controlled release of encapsulated inhibitors. The major strength of these coatings lies in their ability to offer active corrosion protection. Unlike conventional coatings that serve merely as physical barriers, stimulus-responsive coatings can detect changes in environmental conditions (such as pH, temperature, and ions) and release corrosion inhibitors precisely where needed. This intelligent response system, particularly seen in pH-responsive coatings, leverages fluctuations in local pH levels due to corrosion processes to trigger the release of inhibitors, ensuring effective and localized protection against corrosion. This approach not only enhances the longevity of the metal substrates but also offers a more sustainable solution by minimizing the need for frequent reapplication or repair.

Despite the promising advancements, several disadvantages remain. One of the primary concerns is achieving precise control over the stimuli-responsive release behavior, which is crucial for long-term effectiveness. Factors such as the compatibility and dispersion of micro/nanocontainers within the polymer matrix, and the variability in triggering pH values for different metals in diverse environments, can significantly impact performance. Additionally, the potential for uncontrolled release due to external pH fluctuations and the temporary nature of the self-healing effect presented by reversible release mechanisms highlight areas that require further research and development. Compared with the existing literature, stimulus-responsive coatings offer an innovative approach to corrosion protection by integrating the benefits of both organic and inorganic materials through micro/nanocontainers. However, optimizing these coatings for a wider range of applications and environmental conditions remains a critical focus for ongoing research. The challenge lies in balancing the smart responsiveness of the coatings with practical considerations such as compatibility, longevity, and environmental impact. As the field progresses, it is expected that advancements in material science and coating technology will address these limitations, broadening the applicability and effectiveness of stimulus-responsive coatings in metal corrosion protection and beyond.

4.2. Redox-Responsive Coatings Represent a Sophisticated Approach in the Field of Smart Materials, Particularly in the Context of Corrosion Protection

These coatings are engineered to respond to fluctuations in electrochemical potential, a common occurrence during the corrosion process. When local corrosion potential changes due to the presence of corrosive ions, this shift acts as a trigger, initiating the release of encapsulated healing agents and enabling the coating to perform self-healing functions. A key group of materials used in redox-responsive coatings are conducting polymers, which have garnered significant interest due to their unique reversible redox properties [78]. These polymers can be doped with anions, which act as counter ions to the oxidized polymer's main chain [78]. The reduction of the conducting polymer leads to the release of these anions. This change in the polymer's state is accompanied by alterations in its permeability, color, and solubility, among other properties. These physicochemical changes are utilized to control the intelligent release of encapsulated substances in response to redox stimuli. An example of this technology is illustrated by the work of Rohwerder, who developed a self-healing coating using redox-sensitive PANI (polyaniline) capsules [79]. These capsules were loaded with 3-nitrosalicylic acid (3-NisA), a type of corrosion inhibitor. The reversible redox behavior and chemical structure of these PANI capsules were confirmed through cyclic voltammetry (CV) curves in corrosive environments. Additionally, the release of the 3-NisA inhibitors was monitored using UV–vis spectroscopy, which measured absorption at 225 nm under varying electrochemical potentials.

The response of these coatings to different corrosion conditions was simulated by applying specific electrical potentials. A low potential was used to mimic the initiation of corrosion, leading to the reduction of the PANI shell and, consequently, the release of the encapsulated 3-NisA inhibitors. A high potential represented metal passivation and the

reoxidation of the PANI shell by oxygen. In an intact coating without applied potentials, the PANI shell served as an effective barrier, preventing the release of inhibitors. The reduction of the PANI capsules resulted in an increase in capsule volume and shell permeability, facilitating the release of the loaded inhibitors [18]. Conversely, the re-oxidation process decreased permeability, thus preventing further release. These PANI capsules, with their pronounced redox responsiveness, have been successfully incorporated into polymeric substrates to create smart anti-corrosive coatings for zinc substrates. The development of redox-responsive coatings like these represents a significant advancement in materials science, offering dynamic, adaptable solutions for corrosion protection and extending the lifespan and durability of metal substrates in corrosive environments [18].

The advancement of redox-responsive coatings has been significantly bolstered by the development of redox-sensitive nanovalves, a cutting-edge approach in the realm of smart materials. These nanovalves, immobilized on the surfaces of micro/nanocontainers, are pivotal in achieving the controlled, stimulus-responsive release of encapsulated agents. This sophisticated delivery system typically comprises a porous inorganic or hybrid scaffold with switchable gatekeepers mounted on the surface of micro/nanocontainers [79]. These gatekeepers are responsible for opening or closing the pore entrances, thus regulating the on-demand release of the encapsulated agents. These nanovalves often include diverse materials such as inorganic nanoparticles, organic molecules, biological macromolecules, and supramolecular assemblies. Their primary function is to retain the guest molecules within the pores until external stimuli prompt their release. Among these, supramolecular nanovalves on micro/nanocontainer surfaces have garnered substantial research interest. For instance, Fu's group designed redox-trigger smart nanocontainers (RTSNs) by mounting supramolecular switches on the exterior of mesoporous silica nanocontainers (MSNs). These switches undergo a reversible transition between self-complexation and self-dissociation under redox stimuli, enabling controlled release of encapsulated molecules like p-coumaric acid in RTSNs [80].

Electrochemical tests have demonstrated that bilayer coatings, comprising Ce(IV)-doped ZrO_2–SiO_2 sol–gel and RTSN-incorporated ZrO_2–SiO_2 sol–gel, exhibit an excellent self-healing effect [80]. The impedance value of these coatings shows a significant increase in the initial stage, followed by a slight decrease, and finally stabilizes, indicating reliable and long-term active corrosion protection, particularly for aluminum alloys. Another innovative approach involves the use of magnetic Fe_3O_4 as the core in MSNs, as developed by Ding. These MSNs feature supramolecular nanovalves assembled through disulfide bond interactions. When the Mg alloy substrate is damaged by corrosive ions, the surface potential drops, triggering the breakdown of disulfide bonds in the nanovalve and releasing encapsulated 8-HQ inhibitors [81]. The application of a magnetic field ensures uniform dispersion of these micro/nanocontainers near the metal surface, enhancing the coating's quick self-healing function upon local corrosion. Quantum dots have also gained attention as capping gates due to their ease of preparation, biocompatibility, and evident stimulus-responsive features. Sun's design of hollow mesoporous silica sphere nanocontainers with redox-responsive ZnO quantum dots exemplifies this. These nanocontainers release MBT corrosion inhibitors in response to specific environmental stimuli, with the release amount increasing with higher concentrations of reducing agents. Furthermore, Li embedded disulfide bonds in hollow mesoporous organosilica nanoparticles, enhancing the responsive release characteristic of MBT inhibitors under reduction conditions [82]. The incorporation of these nanocontainers in coatings significantly inhibits metal substrate corrosion, as indicated by electrochemical tests. In summary, the embedding of nanovalves on the surfaces of micro/nanocontainers is a crucial step toward minimizing premature release of encapsulated agents and reducing side effects on the coating matrix. The dynamic, reversible, and controllable nature of these nanovalves offers promising prospects for designing intelligent, stimulus-responsive self-healing coatings. This approach represents a significant leap in material science, paving the way for more efficient and durable protective coatings in various applications.

Redox-responsive coatings represent an innovative advancement in smart material science, particularly for corrosion protection. These coatings are designed to react to changes in electrochemical potential, commonly associated with the corrosion process. The deployment of conducting polymers within these coatings, notable for their reversible redox properties, marks a significant stride in materials technology. These polymers, when reduced, facilitate the release of encapsulated healing agents, thus enabling a self-healing function that is critically responsive to corrosive environments.

The main advantage of redox-responsive coatings lies in their dynamic adaptability to the corrosive environment, offering a sophisticated, targeted approach to corrosion protection. By utilizing conducting polymers that undergo reversible redox reactions, these coatings can effectively control the release of encapsulated substances in response to specific electrochemical stimuli. This ensures that healing agents are released precisely where and when needed, directly at the sites of potential or active corrosion, enhancing the durability and lifespan of metal substrates. Moreover, the implementation of redox-sensitive nanovalves on the surfaces of micro/nanocontainers within these coatings has further bolstered their efficacy. These nanovalves, capable of controlling the release of encapsulated agents through reversible transitions under redox stimuli, represent a cutting-edge approach in the design of intelligent, stimulus-responsive self-healing coatings.

Despite these advancements, there are notable challenges to the widespread application of redox-responsive coatings. One significant issue is the complexity involved in engineering these materials to ensure precise control over the redox-triggered release mechanism. Additionally, the compatibility and dispersion of these micro/nanocontainers within the polymer matrix of the coatings must be carefully managed to prevent aggregation and ensure effective barrier properties. Furthermore, the specificity of the redox triggers and the potential for uncontrolled release under fluctuating electrochemical conditions present additional hurdles to achieving consistent, long-term corrosion protection. Compared to existing literature, redox-responsive coatings offer a more dynamic and adaptable solution to corrosion protection, moving beyond the passive barrier mechanisms of traditional anti-corrosive coatings. However, the challenges highlighted underscore the need for continued research and development. Addressing these issues is crucial for optimizing the performance of redox-responsive coatings and expanding their application across a broader range of environmental conditions and metal substrates. As the field progresses, it is anticipated that innovations in material synthesis, nanovalve design, and polymer technology will overcome current limitations, paving the way for more efficient and durable protective coatings.

4.3. Ions-Responsive Coatings Represent a Novel Class of Smart Materials That Are Tailored to Respond to Specific Aggressive Ions Present in Corrosive Environments

These coatings utilize ion-responsive micro/nanocontainers that can rapidly release encapsulated active inhibitors to repair damaged areas on the coating surface. Such coatings are particularly useful in combating microbiologically influenced corrosion, often encountered in marine environments. A notable example of this technology is the work of Cai, who developed S^{2-} ions-responsive nanocontainers by integrating ZIF-8 nano-valves on the surface of mesoporous silica nanocontainers (MSNs). These nanocontainers are sensitive to fluctuations in S^{2-} ion concentrations, which are indicative of sulfate-reducing bacteria activity—a common cause of microbiological corrosion in marine settings. When S^{2-} concentration exceeds a certain threshold, the ZIF-8 nanovalve dissolves, triggering the release of metronidazole inhibitors (Figure 7) [83]. The effectiveness of these smart coatings has been demonstrated, showing significant resistance to microbiologically influenced corrosion, thus highlighting their potential for marine applications. Layered double hydroxides (LDHs) are another group of materials gaining attention in the development of ion-responsive coatings [84]. LDHs have a unique layered structure of cations and anions, with the latter being exchangeable (Figure 8). This property enables the release of anionic inhibitors entrapped within the LDH in response to corrosive anions, proceeding via an

ion-exchange reaction. This exchange traps the corrosive ions within the LDH structure while simultaneously releasing the inhibitors. Mg-Al LDH and Zn-Al LDH are among the most studied LDH materials [85]. Research in this area includes the synthesis of Mg-Al-based LDH coatings intercalated with 8-HQ inhibitors on AZ31 Mg alloys [84,85]. These coatings exchange corrosive Cl- ions with 8-HQ inhibitors, leading to the formation of a protective Mg $(HQ)^2$ chelate layer that inhibits corrosion.
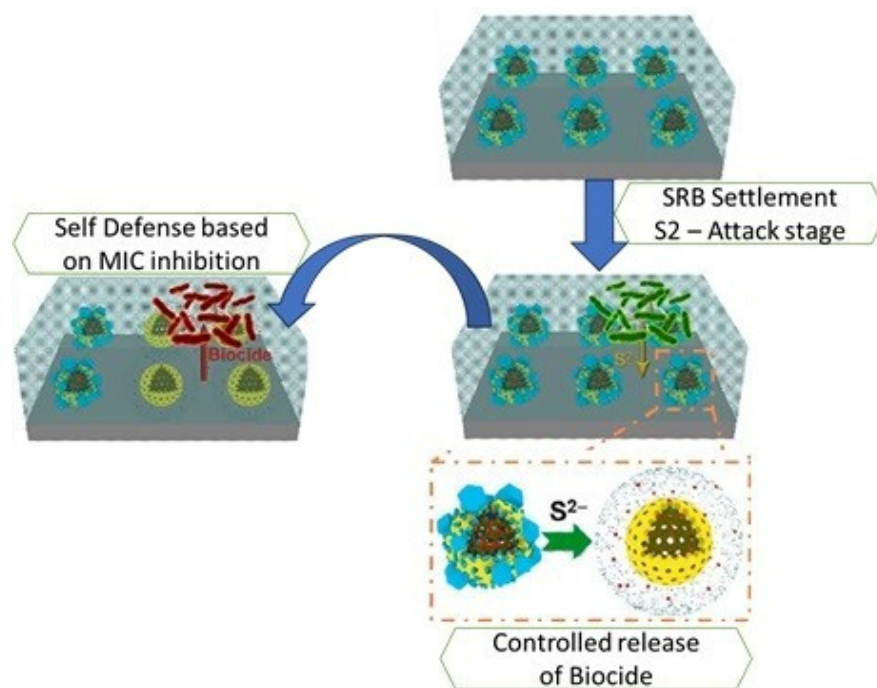
Figure 7. Illustrates how intelligent coatings protect against microbiological corrosion, specifically from sulfate-reducing bacteria (SRB). It shows the process where sulfide ions from SRB activity break down ZIF-8 structures in the coating, a metal-organic framework known for encapsulating substances. This breakdown releases biocides that diffuse through the coating to neutralize SRBs on the metal surface, preventing further corrosion. The figure highlights the coating's ability to detect microbial activity and release biocides, maintaining metal integrity. Reprinted/adapted with permission from Ref. [11]. 2023, Elsevier.

Significant research has been conducted to design various LDHs for active corrosion protection of metals, intercalating both organic and inorganic corrosion inhibitors into the LDHs [85]. These include 2-mercaptobenzothiazolates, quinaldate, 5-aminoindazole, aminobenzoate, thiophene, 8-HQ, aliphatic carboxylates, phenylphosphonic acid, nitrate, vanadate, fluorine, and others [11]. The entrapped inhibitors are released during the ion-exchange process, effectively inhibiting further corrosion of the metal substrate (Figure 9). Despite these advancements, ion-responsive coatings face limitations. Their effectiveness is contingent upon the presence of specific ions in the environment, which narrows their application range [11]. Furthermore, the sensitivity of these coatings to specific ions needs improvement. Also, while the pure LDHs themselves exhibit some protective abilities, the synergistic effects of LDH and encapsulated inhibitors require further investigation. In summary, ion-responsive micro/nanocontainers offer a promising approach to mitigating corrosion processes by effectively capturing corrosive ions [11]. However, the need for specific corrosive environments and the limitation to particular ions underscore the need for continued research and development to broaden the application range and enhance the sensitivity of these innovative coatings.
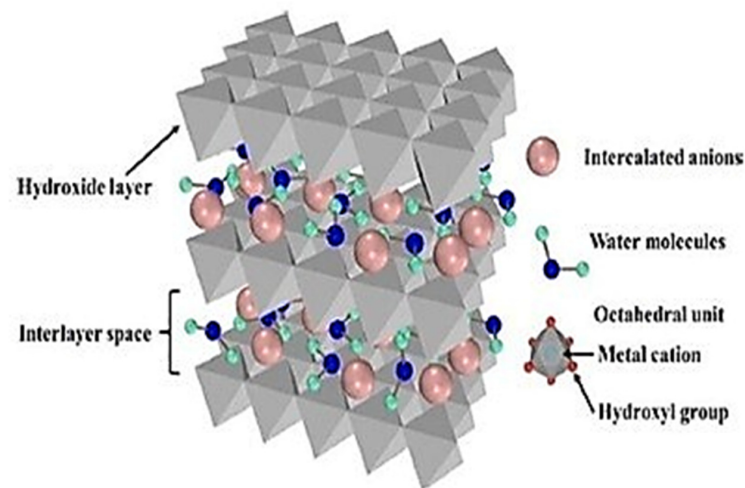
Figure 8. Presumably illustrates the crystalline structure of layered double hydroxides (LDHs), materials known for their brucite-like layered configuration. The diagram depicts stacked layers of octahedrally coordinated metal cations (e.g., magnesium, aluminum, zinc) with hydroxide ions, carrying a net positive charge. The interlayer space, filled with anions, water molecules, and sometimes organic compounds, is negatively charged, balancing the structure. It may also illustrate hydrogen bonding and anion exchange capabilities, crucial for LDHs' uses in adsorption, catalysis, and material synthesis. Annotations could detail layer distances, metal ion arrangement, and other structural characteristics essential for understanding LDHs' properties. Reprinted/adapted with permission from Ref. [84]. 2022, Elsevier.
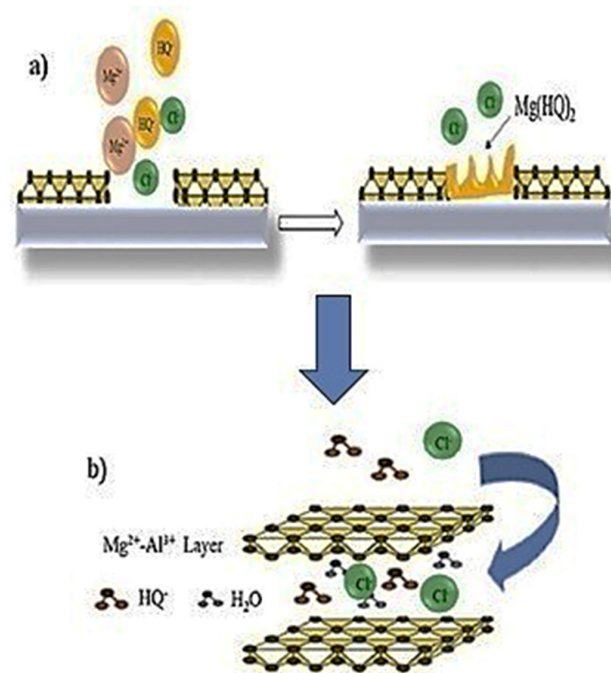
Figure 9. (**a**) Outlines the corrosion protection offered by LDH-based coatings, showing their ability to exchange interlayer ions with corrosive anions (e.g., chloride) from the environment, thus removing these agents from the metal surface. It also illustrates the release of 8-hydroxyquinoline (8-HQ) from LDH layers, which forms a chelate complex with metal ions at corrosion sites, blocking further corrosion. This dual-action mechanism—ion exchange and chelation—highlights the advanced, self-healing properties of LDH coatings in preventing corrosion. (**b**) (The intercalated ions in LDH exchange with corrosive ions, and the entrapped 8-HQ releases and interacts with Mg2+ ions to form chelate to block the active sites). Reprinted/adapted with permission from Ref. [85]. 2022, Springer.

Ion-responsive coatings mark a notable advancement in smart material science, specifically designed to counteract the effects of aggressive ions in corrosive environments. These coatings employ ion-responsive micro/nanocontainers capable of swiftly releasing active inhibitors to mend damaged areas on the surface. This capability is especially crucial for addressing microbiologically influenced corrosion, commonly seen in marine settings. Through the incorporation of innovations such as ZIF-8 nanovalves on mesoporous silica nanocontainers (MSNs), these coatings can detect and respond to specific ion fluctuations, such as S2- ions associated with sulfate-reducing bacteria activity, a prevalent cause of microbiological corrosion in marine environments. The primary advantage of ion-responsive coatings lies in their targeted response to specific ions, allowing for the direct and efficient mitigation of corrosion processes. This specificity is particularly valuable in environments like marine settings, where microbiologically influenced corrosion poses a significant threat. The integration of innovative materials like LDHs, with their unique layered structure and ion-exchange capabilities, further enhances these coatings' ability to trap corrosive ions while releasing protective inhibitors, thus providing a double-action protective mechanism against corrosion.

However, the application of ion-responsive coatings is not without its limitations. Their effectiveness is heavily reliant on the presence of specific ions, narrowing their applicability to environments where such ions are prevalent. Additionally, the sensitivity of these coatings to detect and respond to specific ion concentrations requires further improvement to ensure consistent and reliable corrosion protection. Moreover, while LDHs themselves offer some level of protection, the exploration of their synergistic effects with encapsulated inhibitors needs more extensive research to optimize the coatings' overall protective capabilities. Compared to the existing literature, ion-responsive coatings represent a promising yet relatively niche solution to corrosion protection. The need for specific environmental conditions and the challenge of achieving broad-spectrum applicability highlight the importance of ongoing research. Future developments should focus on enhancing the sensitivity and range of ions these coatings can respond to, as well as exploring the potential of various LDHs and other ion-responsive materials for broader application. By addressing these challenges, ion-responsive coatings have the potential to become a more universally applicable solution for corrosion protection across diverse environmental conditions.

4.4. Light-Responsive Coatings

The study of light-responsive coatings, particularly for metal corrosion protection, centers around incorporating photosensitive elements that activate photochemical reactions upon light absorption. These materials have recently made strides in the field of corrosion protection, leveraging the alteration in electron density of photocatalytic substances under UV light to modulate corrosion protection efficiency innovatively. A prevalent strategy in designing these smart coatings involves using photocatalytic substances like TiO_2, WO_3, and CdS. For example, He [86] engineered a photocatalytic self-repairing coating by integrating 8-HQ inhibitors within TiO_2 nanoparticles, subsequently wrapped in a polyethyleneimine shell. Exposure to UV light (260 nm) instigates the release of these inhibitors, thereby establishing a protective barrier on the metal surface to curb further corrosion. In a parallel development, Ma [87] fabricated a dual light and thermal responsive coating employing $TiN@SiO_2$ nanocontainers imbued with BTA inhibitors. These nanocontainers, when merged with a shape memory epoxy coating, discharge inhibitors under NIR irradiation. The photothermal effect of TiN nanoparticles plays a dual role in releasing inhibitors and activating the shape memory feature for scratch repair.

These coatings have demonstrated significant corrosion resistance enhancement, evidenced by substantial impedance value increases. We also discuss the innovative use of azobenzene molecules in coatings where light manipulation can control inhibitor release. Recent research has expanded to include materials like carbon, noble metals, Fe_3O_4, MXene, and aniline black, known for their robust photothermal effects under light exposure. These materials effectively transform light into heat, impacting the coatings' characteristics. A notable example is Li's [88] creation of UV-responsive microcapsules filled with NIR-

responsive carbon nanoparticles, forming part of self-healing superhydrophobic coatings. In summary, light-responsive self-healing coatings represent a breakthrough in metal corrosion protection, offering remote, targeted activation and rapid response capabilities. These coatings extend beyond mere protective functions, encompassing self-repair abilities and demonstrating the vast potential of light-responsive technologies across various sectors.

The application of photochromic molecules, such as ortho-nitrobenzyl, coumarin, azobenzene, and spiropyran-based polymers, is a well-known technique due to their rapid and reversible photoisomerization properties. For example, Chen's research [89] introduced an innovative light-triggered anti-corrosive coating. This was achieved by incorporating azobenzene molecules into mesoporous silica nanoparticles (MSNs). The azobenzene-MSNs were then dispersed in water-borne alkyd coatings. Under visible light, the azobenzene molecules transitioned from their cis to trans isomer, effectively acting as a "gatekeeper" to block the diffusion of encapsulated inhibitors. Conversely, UV light exposure (at 365 nm) reverted the azobenzene from its trans form back to the cis form, facilitating the release of the molecules. This transformation can also be achieved by visible light at 450 nm, which reverts the cis form back to the trans form, closing the MSN surface pores and halting the release process. Local current density tests validated the precise control over the release of azobenzene, confirming the coating's capability for photosensitive self-healing, thereby enhancing long-term protection of substrates, even after repeated damage (Figure 10).
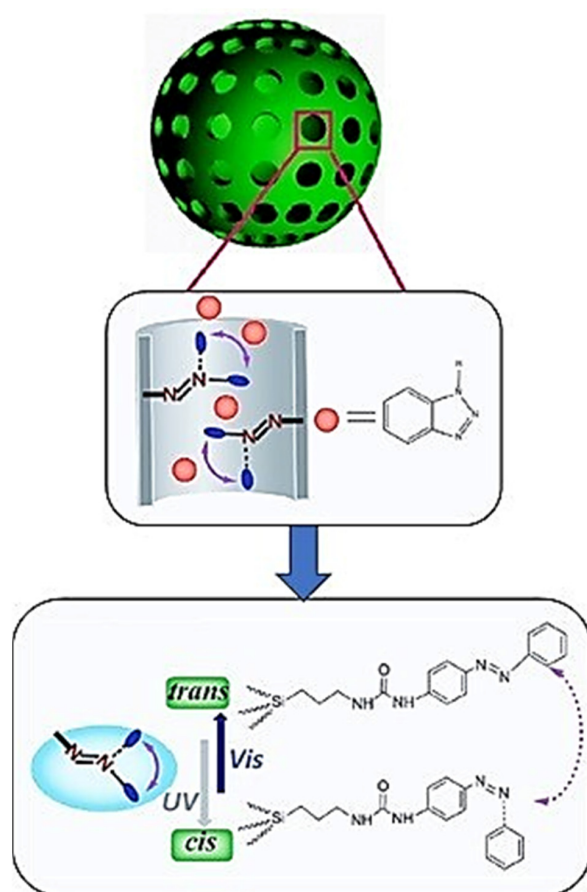
Figure 10. The illustration shows how azobenzene molecules on mesoporous silica nanoparticles (MSNs) change shape under different light wavelengths through photoisomerization. Under UV light (365 nm), azobenzene shifts from trans to cis configuration, opening MSN pores for controlled cargo release. Visible light (450 nm) reverses this to trans, closing the pores and stopping release. This mechanism, depicted with molecular structures and pore changes, highlights the smart, externally controllable delivery system.

Further research indicates that various materials like carbon, noble metals (silver, gold, gold sulfide, gold nanorods, etc.), Fe_3O_4, MXene, and aniline black exhibit significant photothermal effects under light irradiation. This phenomenon allows the conversion of light energy into heat, influencing the structure or physicochemical properties of polymeric shell materials. For instance, Li [88] developed UV-responsive microcapsules integrated with NIR-responsive carbon nanoparticles. These nanoparticles, mixed into waterborne silicone latex along with silica nanoparticles, create self-healing superhydrophobic coatings. Upon UV irradiation, the carbon nanoparticles generate heat, melting the microcapsules and releasing 1H, 1H, 2H, and 2H-perfluorooctyltriethoxysilane inhibitors. These inhibitors then migrate to the metal surface, restoring its superhydrophobic characteristics. The light stimulus stands out among external stimuli sources for its ability to remotely activate self-healing coatings, enabling nondestructive repair of selected damaged areas in an ultrafast process. This design principle extends beyond corrosion protection, as light-responsive micro/nanocontainers and coatings are also crucial for the controlled release of various active agents in different applications.

Light-responsive coatings represent a cutting-edge development in smart materials, especially within the sphere of corrosion protection for metals. These coatings are ingeniously designed to react to light exposure—particularly UV light—by activating photochemical reactions that lead to the release of encapsulated corrosion inhibitors. This innovative approach not only promises enhanced corrosion resistance but also introduces the potential for self-repairing capabilities in the coatings. One of the primary benefits of light-responsive coatings lies in their ability to provide remote, targeted activation and a rapid response to environmental changes. The incorporation of photocatalytic substances like TiO_2 into these coatings leverages the alteration in electron density under UV light, ingeniously modulating the corrosion protection efficiency. This feature allows for the on-demand release of inhibitors, precisely when the metal surface encounters corrosive threats, thereby offering a proactive approach to corrosion protection. Furthermore, the versatility of these coatings, demonstrated by their application in dual light and thermal responsive systems, showcases the breadth of their potential utility beyond mere corrosion resistance, encompassing self-repair and even scratch repair functionalities.

However, the deployment of light-responsive coatings also comes with its set of challenges. The reliance on specific wavelengths of light to trigger the release mechanisms might limit the coatings' effectiveness in environments with limited light exposure. Additionally, the complexity involved in integrating photocatalytic substances and ensuring their uniform distribution within the coating matrix poses significant technical hurdles. Moreover, the durability of these light-triggered mechanisms under continuous or prolonged exposure to environmental conditions remains a concern, potentially affecting the long-term reliability of the corrosion protection offered. Compared to existing literature, light-responsive coatings mark a notable advancement by introducing an innovative mechanism for corrosion protection that extends beyond the passive barrier methods traditionally employed. These coatings' dynamic adaptability and self-healing capabilities represent a significant leap forward. However, addressing the challenges related to light dependence, material integration, and long-term durability is crucial for optimizing these smart coatings' performance. As research in this area progresses, further innovations in material science and coating technology are expected to enhance the practical applicability and effectiveness of light-responsive coatings in various industrial and environmental settings.

4.5. Thermo-Responsive Coatings

Thermo-responsive coatings, a pivotal innovation in corrosion protection, utilize materials capable of transforming light energy into heat. This transformation facilitates a rapid release of internal energies, increasing surface temperatures. Central to this technology are shape memory polymers (SMPs), which exhibit remarkable thermo-sensitivity. SMPs can revert to their pre-deformed shape when subjected to external heat, a feature underpinned by their unique molecular mechanisms. These polymers, encompassing

polyolefins, polyethers, polyesters, and particularly polyurethane, serve as versatile coating matrices, accommodating various inhibitors or microcapsules. The self-healing effectiveness of SMPs is underlined, especially in addressing surface micro-defects. However, their efficacy is contingent on their inhibitor loading and leaching capacities. Li's group pioneered the "close-then-heal" strategy to extend this self-healing capability to larger defects. This method employs heat to induce molecular chains to return to a lower energy state, facilitating the coating's self-closure. Graphene oxide, noted for its photothermal conversion ability, has been harnessed in developing advanced SMP coatings (Figure 11). Cheng [90] innovatively integrated polydopamine at graphene oxide with specific agents into an SMP matrix, achieving swift self-healing upon NIR irradiation and introducing a sensing function through the formation of a Phen-Fe complex.
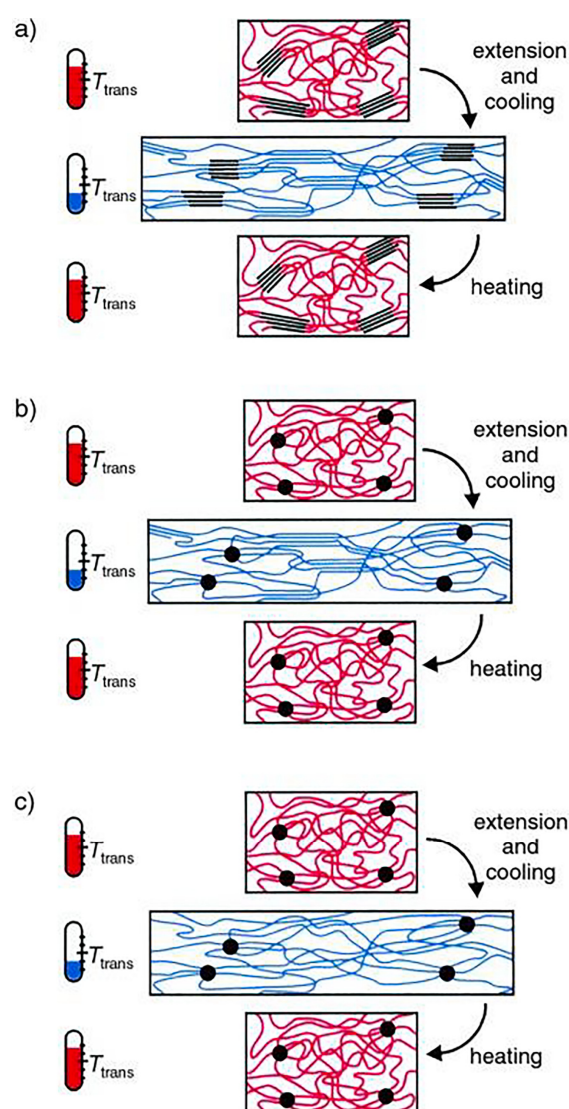
Figure 11. Illustrates the molecular mechanisms in shape memory polymers (SMPs), polymers that return to their original shape when exposed to stimuli like heat. Part (**a**) shows a multiblock copolymer's structure with alternating polymer segments, each providing unique thermal and elastic properties for shape memory. Part (**b**) depicts a covalently cross-linked polymer, with cross-link junctions (black dots) and molecular chains represented by blue lines (low mobility below transition temperature, T_trans) and red lines (high mobility above T_trans). Part (**c**) displays a polymer network deformable below its melting point (T_m) and recoverable above T_trans, highlighting SMPs' shape recovery process and underlying molecular transitions. Reprinted/adapted with permission from Ref. [91]. 2023, Springer.

To amplify the healing efficiency and embrace the dual benefits of the close-then-heal approach, thermoplastic fillers have been incorporated into SMPs. Huang [91] developed new SMP coatings with microspheres containing poly (ε-caprolactone) and inhibitors. These coatings demonstrated enhanced healing capabilities and maintained corrosion resistance upon heating. Luo [92] furthered this concept with SMP coatings containing thermoplastic poly (ε-caprolactone) fibers, facilitating the connection of cracked areas through melting and flow. In summary, these innovative thermo-responsive coatings leverage the close-then-heal mechanism and the integration of micro/nanocontainers to deliver a comprehensive self-healing solution (Figure 12). This approach not only retains the coating's integrity but also effectively counters the ingress of corrosive elements, demonstrating remarkable potential in efficiently addressing corrosion at a molecular level.
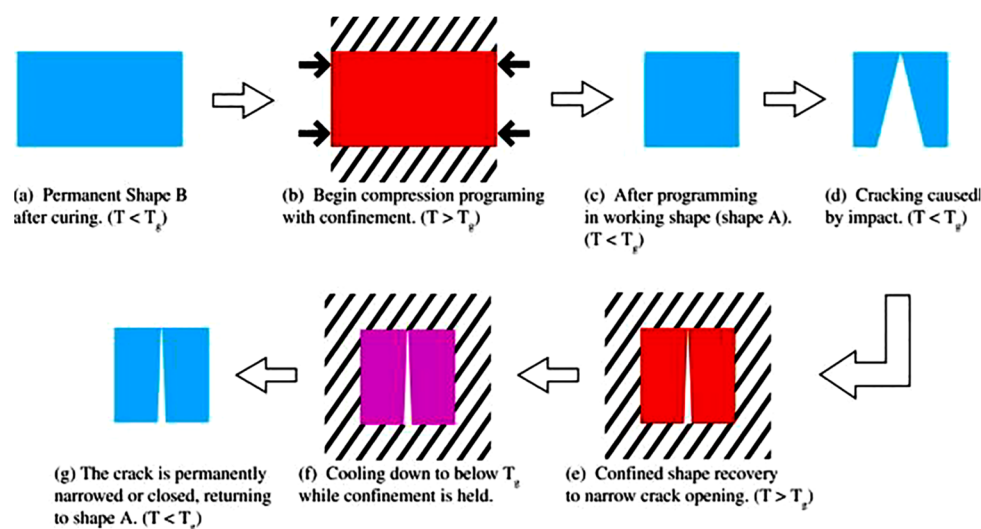
Figure 12. Represents how a shape memory polymer (SMP) returns from a temporary to its original shape upon reaching its glass transition temperature (Tg), where it shifts from a hard state to a more ductile one. Initially depicted in a deformed state below Tg with frozen polymer chains, the figure illustrates the SMP gaining mobility as temperature rises above Tg, enabling it to "self-close" back to its memorized shape. Annotations explain temperature stages, polymer chain configurations, and SMP interactions during this transformation, highlighting its use in self-adjusting or repairing systems in fields like aerospace and biomedical devices. Reprinted/adapted with permission from Ref. [92]. 2019, RSC Publishing.

In an innovative study, Cheng [90] developed a multifunctional thermal-responsive shape-memory polymer (SMP) coating. This coating was uniquely engineered by embedding polydopamine-coated graphene oxide, which was further loaded with 1,10-phenanthrolin-5-amine. The SMP coating stands out for its rapid self-healing ability, which is activated within just 90 s of exposure to near-infrared (NIR) irradiation. This quick response is attributed to the unique properties of the materials used. Polydopamine provides a strong adhesion to the graphene oxide, enhancing the coating's stability and durability. Graphene oxide contributes to the thermal-responsive nature of the coating, while 1,10-phenanthrolin-5-amine plays a crucial role in the healing process. A remarkable feature of this SMP coating is the formation of a Phen-Fe complex, which imparts a sensing function to the coating (Figure 13). This complex is responsible for the coating's ability to detect and respond to environmental changes, particularly in terms of temperature variations. In practical applications, when the coating is scratched, the NIR healing process is triggered, effectively repairing the damage. The effectiveness of this self-healing feature was demonstrated through an experiment where the scratched coatings were exposed to a 3.5 wt% NaCl solution for 15 days. The results were impressive, showing a high impedance value of $4.15 \times 10^5 \ \Omega \cdot cm^2$ after the immersion period. This high impedance indicates a strong

resistance to corrosion and damage, underscoring the coating's excellent self-repairing performance. Cheng's creation of this smart SMP coating is not only significant for its rapid self-healing capability but also for its ability to handle wide scratches and provide durable protection in harsh environments. This innovation holds great promise in various applications, particularly in fields requiring materials with high durability, self-healing properties, and environmental responsiveness. The combination of thermal responsiveness, rapid self-healing, and sensing capabilities makes this SMP coating a groundbreaking advancement in smart material technology.
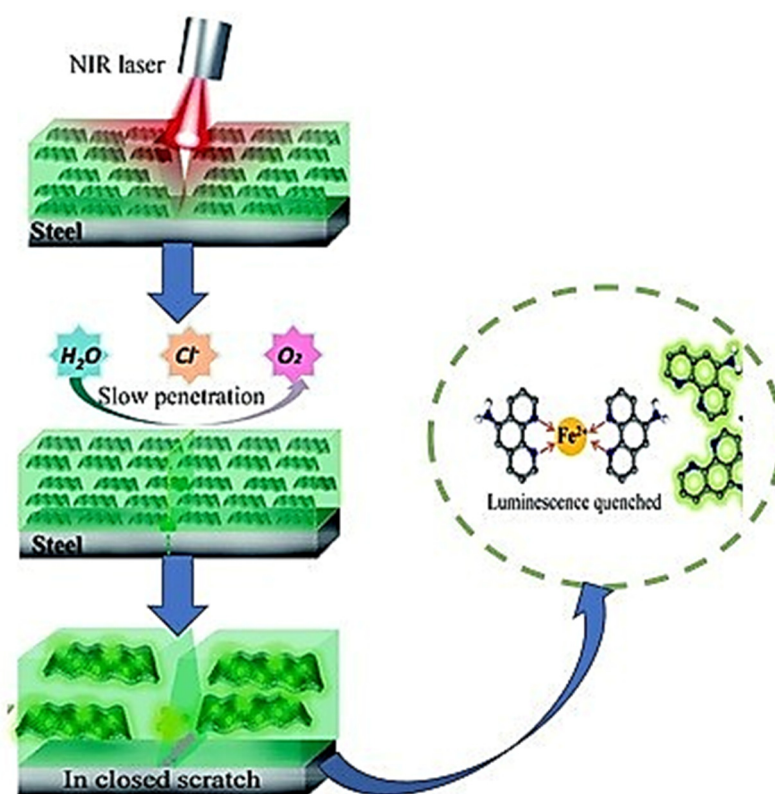
Figure 13. Indicates a self-sensing SMP coating with a close-then-heal mechanism. Triggered by NIR irradiation, the coating incorporates polydopamine and graphene oxide, which convert NIR to thermal energy, prompting the SMP to revert from deformed to original form, closing superficial damage like scratches. Then, 1,10-phenanthrolin-5-amine mobilizes into damaged areas during the shape memory response for self-sensing, indicating repair. This dual-action process, combining self-repair and damage detection, is crucial for applications requiring continuous integrity monitoring, such as structural health systems. Reprinted/adapted with permission from Ref. [90]. 2021, RSC Publishing.

Thermo-responsive coatings, leveraging shape memory polymers (SMPs) and photothermal materials like graphene oxide, represent a significant leap forward in corrosion protection technologies. These innovative coatings are designed to respond to temperature changes, enabling them to repair damage autonomously, which is crucial for protecting metal substrates from corrosion. The primary advantage of thermo-responsive coatings is their ability to self-heal. Utilizing SMPs that can revert to their original shape upon heating allows these coatings to close cracks and repair damage without manual intervention, thereby preserving the integrity of the underlying metal. The incorporation of materials with photothermal conversion capabilities, such as graphene oxide, further enhances these coatings by enabling rapid self-healing upon exposure to specific light wavelengths. This dual mechanism of action—thermal responsiveness for healing and photothermal effects for rapid activation—provides a robust defense against corrosion. Furthermore, the addition of

thermoplastic fillers to SMPs has been shown to improve the healing efficiency, offering a close-then-heal approach that extends the coatings' self-healing capability to larger defects.

However, several challenges accompany thermo-responsive coatings. Their effectiveness heavily relies on the specific materials used, their inhibitor loading capacity, and the precision in activating the self-healing process. Achieving uniform dispersion of micro/nanocontainers within the SMP matrix and ensuring their stable integration without compromising the coating's physical properties are critical yet complex tasks. Additionally, the dependency on external heat sources to trigger the healing process may limit the applicability of these coatings in environments where such control is not feasible. Compared to the existing literature, thermo-responsive coatings offer a more dynamic and adaptable solution for corrosion protection. The innovative close-then-heal strategy, combined with the integration of micro/nanocontainers, sets them apart from traditional corrosion protection methods, which are typically passive and do not possess self-healing capabilities. However, the need for further research to optimize the materials used, improve the efficiency of the healing process, and expand the applicability of these coatings is evident. Future developments in this field are expected to address these challenges, enhancing the performance of thermo-responsive coatings and broadening their use in various environmental conditions and applications.

4.6. Magnetic-Field Responsive Coatings

Magnetic-field responsive coatings, drawing inspiration from drug delivery systems, employ magnetic nanoparticles as carriers to transport active substances to specific areas in the body. In the realm of corrosion protection, these magnetic-field sensitive micro/nanocontainers exhibit significant potential. These containers release encapsulated active substances in response to environmental changes, effectively forming a protective layer on metal surfaces. This process not only offers active corrosion protection but also enables self-repairing functions. A crucial element in the effectiveness of these coatings is the dispersion of the micro/nanocontainers within the coating matrix. The use of magnetic-based micro/nanocontainers is a noteworthy improvement. By applying an external magnetic field, the location and orientation of these containers can be precisely controlled, ensuring more effective and targeted corrosion protection. Magnetic nanoparticles are particularly advantageous for this application due to their high chemical stability, low toxicity, and ease of functionalization. Wang's development of a magnetic poly(urea–formaldehyde) coating, which incorporates BTA inhibitors and multiwall carbon nanotubes, exemplifies this technology's efficacy. The magnetic microcapsules within this coating can be quickly and easily maneuvered under an external magnetic field. This capability not only facilitates the movement of the microcapsules but also shortens the transmission pathway of the released BTA molecules compared to non-magnetic microcapsules, significantly extending the coating's service life. Electrochemical tests have confirmed the high inhibition efficiency of this coating, with a self-healing magnetic coating reaching an impressive 91.2% efficiency within four hours of BTA release. When compared to non-magnetic gradient coatings, the magnetic gradient self-healing coating shows a corrosion protection efficiency improvement of approximately 6.4 times.

Beyond corrosion protection, magnetic-based micro/nanocontainers are also valuable in corrosion detection, especially for aeronautical and offshore metallic structures often exposed to aggressive environments. Traditional corrosion monitoring methods are typically complex and costly. However, since corrosion is an electrochemical process involving ion and electron movement, it has an associated magnetic component. Utilizing the magnetic field generated by corrosion currents offers a novel approach to monitoring metal corrosion. Superconducting interference device sensors, for instance, can detect corrosion in large metallic structures, although their broad applicability is currently limited by high costs and low resolution. An innovative method to enhance the sensitivity of current and magnetic flux leakage measurements in corrosion detection involves incorporating magnetic nanoparticles into coatings. These iron-based nanoparticles can alter their magnetic field intensity in response to pH changes, a common occurrence during corrosion. This varia-

tion in magnetic field intensity not only signals the onset of corrosion but also indicates the physical degradation of the coating, making it a vital factor in monitoring corrosion activities and implementing preventive measures.

Magnetic-field responsive coatings represent an innovative approach in the domain of corrosion protection, mirroring strategies from drug delivery systems to harness magnetic nanoparticles for targeted delivery and release of active substances. These advanced coatings are designed to respond to environmental changes, deploying encapsulated active agents to form a protective barrier over metal surfaces, thereby offering both active corrosion protection and self-repair capabilities. The primary advantage of magnetic-field responsive coatings lies in the precise control and targeted delivery of corrosion inhibitors. By leveraging magnetic nanoparticles, these coatings enable the manipulation of micro/nanocontainers' location and orientation within the coating matrix through an external magnetic field. This specificity ensures that corrosion protection is not just effective but also efficient, focusing on areas most in need of repair or protection. Magnetic nanoparticles are celebrated for their high chemical stability, low toxicity, and ease of functionalization, making them an ideal choice for such applications. The ability to quickly maneuver magnetic microcapsules under a magnetic field shortens the transmission pathway of released active substances, enhancing the coating's protective efficiency and extending its service life.

Despite their promising potential, magnetic-field responsive coatings face challenges that limit their widespread application. The requirement for an external magnetic field to activate the release mechanism may not always be practical or feasible in all operational environments. Moreover, ensuring uniform dispersion of magnetic micro/nanocontainers within the coating matrix to prevent agglomeration and maintain the integrity of the protective layer poses significant technical challenges. Additionally, the cost and complexity of integrating magnetic nanoparticles into coatings can be higher compared to non-magnetic systems, potentially hindering their adoption in cost-sensitive industries. Compared to the existing literature, magnetic-field responsive coatings offer a more dynamic and targeted approach to corrosion protection, surpassing traditional methods that act as passive barriers. However, the practicality of applying external magnetic fields and the cost implications of using magnetic nanoparticles necessitate further research and development. Future innovations are expected to focus on overcoming these limitations, enhancing the practical applicability of magnetic-field responsive coatings and broadening their use across various industries exposed to corrosive environments.

4.7. Multistimulus-Responsive Coatings

Multistimulus-responsive coatings represent a significant advancement in the field of smart materials, especially in applications like corrosion protection. These innovative coatings are designed to rapidly respond to various environmental factors, providing active corrosion protection and self-healing effects. While past research has focused largely on single stimulus-responsive mechanisms, achieving remarkable breakthroughs, the complexity of real-world corrosive environments necessitates the development of coatings that can respond to multiple stimuli simultaneously. This need for multistimulus adaptability has led to the creation of coatings that can react to different triggers, such as changes in pH, temperature, and redox conditions. For instance, Li [93] developed silica/polymer doublewall hybrid nanotubes that were surface-grafted with three different polyelectrolytes—each responsive to a different stimulus (pH, temperature, or redox). These nanotubes, when incorporated into silica-zirconia sol–gel coatings, demonstrated an excellent ability to respond to the three stimuli, showcasing a notable self-healing effect (Figure 14).

Conducting polymers have also been explored for their adjustable conductivity and eco-friendly anti-corrosive properties. Saremi [94] encapsulated molybdate inhibitors in mesoporous silica, which were then dispersed in polypyrrole (PPy) coatings. These coatings released greater amounts of molybdate inhibitors in environments with high pH and chlorine concentrations, indicative of their responsive nature. A particularly

innovative approach involves the use of supramolecular valves to create triple stimulus–responsive systems, enhancing both the efficiency of inhibitor usage and self-healing capabilities. Wang [95] developed nanocontainers with BTA corrosion inhibitors, controlled by a bistable pseudorotaxane supermolecular nanovalve. These nanocontainers, when stimulated by acid, base, or corrosion potentials, rapidly released their contents. This design was integrated into SiO_2-ZrO_2 sol–gel coatings to create smart, self-repairing anti-corrosive coatings. These coatings could adapt to changes in micro pH values and corrosion potentials during the corrosion process. The use of supramolecular nanovalves effectively prevented the premature leakage of BTA inhibitors and enhanced the sensitivity of the nanocontainers.
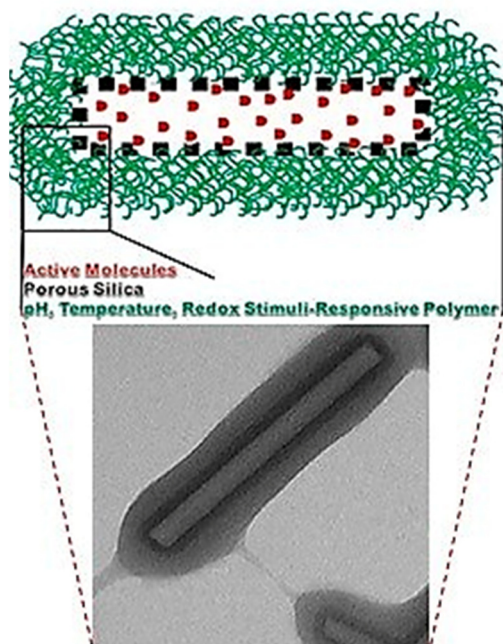
Figure 14. Illustrates double-walled hybrid nanotubes with an inner silica layer for stability and an outer polymer layer for responsive properties to temperature, pH, and specific chemicals or biological agents. The polymer's responsiveness allows the nanotubes to physically or chemically adapt, changing their diameter or charge properties for applications like controlled drug release, chemical sensing, or microfluidic actuators. Visual cues in the schematic show how the nanotubes respond to stimuli, highlighting their potential in high-tech applications. Reprinted/adapted with permission from Ref. [93]. 2013, ACS Publications.

Multistimulus-responsive coatings are set to play a vital role in various industries due to their ability to adapt to a range of environmental changes. Their intelligent and flexible design allows for the selective release of encapsulated payloads in response to specific stimuli, leading to rapid feedback and superior active corrosion protection. However, the development of such sophisticated coatings is not without challenges. The fabrication of multistimulus-responsive micro/nanocontainers typically involves complex, multistep synthesis processes [95]. Therefore, future research should focus not only on developing new types of stimulus-responsive coatings but also on streamlining the synthesis procedures to create these multistimulus-responsive micro/nanocontainers more efficiently and effectively.

Multistimulus-responsive coatings are at the forefront of smart material technology, offering unparalleled advantages in corrosion protection by responding to various environmental triggers. These coatings, capable of reacting to changes in pH, temperature, and redox conditions, represent a significant leap from traditional single stimulus-responsive systems. Their development has been propelled by the need to address the multifaceted nature of real-world corrosive environments, leading to the innovation of coatings that offer active protection and self-healing capabilities through the integration of various responsive elements. The primary benefit of multistimulus-responsive coatings is their versatility. They

can adapt to a wide range of environmental changes, offering targeted and efficient corrosion protection. For instance, coatings that incorporate hybrid nanotubes responsive to pH, temperature, and redox changes can demonstrate self-healing effects, thereby significantly extending the lifespan of metal substrates. Furthermore, the integration of conducting polymers and supramolecular valves into these coatings enhances their responsive nature, allowing for the controlled release of inhibitors and improving the coatings' self-healing capabilities. This intelligent design ensures that the coatings can provide superior active corrosion protection, adapting dynamically to varying conditions.

However, the development of these advanced coatings faces several challenges. The fabrication process of multistimulus-responsive micro/nanocontainers is complex and often involves multistep synthesis procedures, making the production process labor-intensive and potentially costly. Additionally, ensuring the compatibility of different responsive elements within a single coating matrix, without compromising the individual responsiveness of each element, presents a significant challenge. There is also the task of precisely controlling the release of encapsulated agents in response to multiple stimuli, which requires sophisticated design and testing to achieve optimal performance. Compared to the existing literature, multistimulus-responsive coatings mark a significant advancement by offering a more comprehensive approach to corrosion protection. While past research has made considerable strides in single-stimulus systems, the dynamic and complex nature of real-world environments necessitates coatings that can respond to multiple triggers. Future research in this field should aim not only at innovating new types of stimulus-responsive materials but also at refining the synthesis processes to make the production of these advanced coatings more practical and scalable. By addressing these challenges, multistimulus-responsive coatings have the potential to revolutionize corrosion protection across various industries, providing a smarter, more adaptable, and more efficient solution to metal preservation.

5. Application of the Micro/Nanocontainers in Functional Coatings

The application of micro/nanocontainers in the field of functional coatings represents a significant advancement in modern material science and technology. These micro/nanocontainers are tiny vessels capable of holding active substances, and their use spans across various domains, including but not limited to drug delivery, food preservation, energy storage and conversion, catalysis, and especially protecting metals against corrosion. These containers are characterized by their intelligent behavior, which is predominantly showcased through their ability to respond to external stimuli. When exposed to specific environmental triggers, these micro/nanocontainers promptly react by releasing the substances they contain. This release mechanism is finely tuned and stimulus-responsive, ensuring that the active agents are discharged only when necessary. Once released, these agents permeate into minute areas within the coatings, where they play a critical role in repairing and maintaining the coating's integrity. This smart release process not only contributes to active corrosion protection but also extends the life and enhances the performance of the coatings [16,18].

The versatility and efficacy of these coatings are largely dictated by the nature of the substances encapsulated within the micro/nanocontainers. The potential for multi-functionality in these intelligent coatings is vast, depending on what is loaded into the containers. For instance, incorporating fluorescent materials results in coatings that possess a self-reporting capability, which is crucial for monitoring and maintenance purposes. Similarly, embedding anti-bacterial agents imparts the coatings with the ability to resist microbial growth, thereby maintaining hygienic surfaces. The paper also delves into other functionalities like anti-fouling, self-lubrication, and self-healing properties, which further broaden the scope and application of these smart coatings. Each of these properties contributes to a coating's ability to protect and preserve the underlying material while also introducing new features that can be tailored for specific applications [18].

5.1. Self-Reporting and Self-Healing Coatings

The self-healing coatings, which are innovative solutions in the field of corrosion protection for metals. The primary function of these coatings is to act as a physical barrier, shielding metal surfaces from corrosive ions. However, over time and with prolonged exposure to harsh environments, these coatings inevitably degrade. This degradation can lead to the formation of micro-cracks, which are often difficult to detect but can allow corrosive ions to penetrate and reach the metal surface, thus accelerating both the degradation of the coating and the corrosion of the metal. Recent developments have led to the emergence of "self-reporting coatings", designed to detect micro-defects early in the corrosion process [16]. These smart coatings typically incorporate fluorescent compounds or color-changing dyes, which are sensitive to changes associated with corrosion. These changes can include local pH variations due to anodic or cathodic corrosion reactions. The dyes or compounds respond by changing color or fluorescing, thereby "reporting" the onset of corrosion. To prevent premature activation or interference with the coating matrix, these indicators are often encapsulated in micro/nanocontainers [12].

The incorporation of these indicators has significantly improved the performance of coatings, providing comprehensive, active corrosion protection for metals. For instance, certain fluorescent molecules, when released from damaged microcapsules in the coating, produce a bright fluorescence, signaling the presence of cracks or damage (Figure 15). Furthermore, the sensitivity of these coatings can be enhanced by selecting specific fluorophores that respond to metal ion complexation, making them more effective than colorimetric indicators. These properties are advantageous for detecting corrosion in various types of coatings, whether transparent or opaque. However, factors such as the amount of fluorophore incorporated and the method of encapsulation can impact the overall properties of the coating. To improve practical applicability, some self-reporting coatings use color indicators, which provide easier visual inspection than fluorescence. These indicators change color at the onset of corrosion, offering a straightforward method for monitoring the integrity of the coating [7,16]. Various researchers have developed coatings with such indicators, demonstrating their effectiveness in early corrosion detection and their superior self-healing abilities under different conditions.
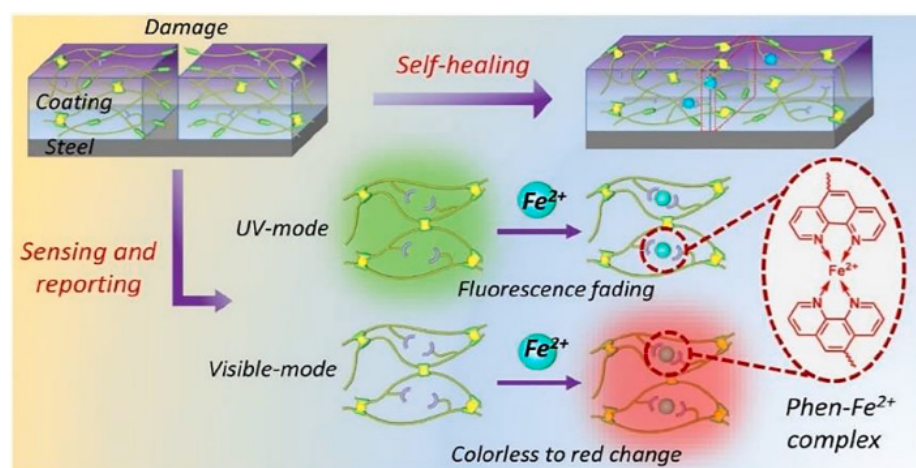
Figure 15. Shows a schematic representation of a material with self-healing and self-reporting functions. The self-reporting is marked by an intense red color and reduced fluorescence at damage sites due to the Phen-Fe complex formation, signaling the need for healing. The schematic details the Phen-Fe complex's molecular structure and optical signature. Self-healing occurs through dynamic hydrogen bonds in the material's matrix, allowing it to mend autonomously. This process is reversible and repeatable, enhancing durability. The diagram highlights intermolecular interactions and the healing process, underlining the material's autonomous restoration capability, valuable in aerospace, electronic skins, or smart coatings. Reprinted/adapted with permission from Ref. [94]. 2021, Elsevier.

Among these indicators, Phenolphthalein (PhPh) has been identified as an effective pH indicator due to its distinct color change over a specific pH range. Coatings with PhPh-loaded nanocapsules have shown promising results in early corrosion detection tests, outperforming coatings with directly dispersed Ph. Recent studies have also explored the use of fluorescent molecules with aggregation-induced emission (AIE) in self-reporting coatings [20,24]. These AIE molecules, when released from ruptured micro/nanocontainers in damaged areas of the coating, aggregate and become visible to the naked eye. Such AIE-based systems offer a simple, fast, and sensitive mechanism for detecting coating damage and assessing corrosion. Despite these advancements, there are still challenges and limitations to be addressed in the development of self-reporting coatings. Issues such as the selection of appropriate indicators for different environments, coating thickness, stability of color signals, and the reversibility of the response are critical for enhancing the reliability and effectiveness of these coatings. Additionally, the synthesis technology of microcapsules, the amount of AIE molecules incorporated, and their sensitivity are areas that require further exploration.

The integration of micro/nanocontainers into functional coatings signifies a substantial progression in materials science, offering innovative solutions for corrosion protection and beyond. These micro/nanocontainers are engineered to release active agents in response to specific environmental stimuli, thereby enhancing the durability and functionality of coatings. One of the primary advantages of utilizing micro/nanocontainers in functional coatings is their ability to provide active and targeted corrosion protection. The stimulus-responsive release mechanism ensures that protective agents are dispensed precisely when needed, minimizing waste and maximizing efficiency. Furthermore, the potential for multifunctionality, depending on the encapsulated substances, broadens the scope of applications for these coatings. From self-reporting capabilities for maintenance monitoring to anti-bacterial properties for maintaining hygienic surfaces, these intelligent coatings offer a versatile platform for addressing a wide array of material challenges.

However, there are challenges to the widespread application of these coatings. The effective dispersion of micro/nanocontainers within the coating matrix and ensuring their stability and compatibility are critical yet complex tasks. Additionally, the precise control over the stimulus-responsive release behavior to ensure long-term effectiveness poses a significant challenge. Moreover, the complexity involved in creating these sophisticated coatings can lead to increased production costs and complexities in scaling up for industrial applications. Compared to traditional coatings that act primarily as physical barriers, micro/nanocontainer-based functional coatings represent a leap forward by offering self-repairing and active protection functionalities. Previous studies have largely focused on single-stimulus systems, but the complexity of real-world applications demands coatings that can respond to multiple environmental factors. While significant advancements have been made, further research is needed to optimize the encapsulation and release mechanisms, improve the compatibility of containers with various coating matrices, and develop cost-effective manufacturing processes. Self-reporting and self-healing coatings, in particular, illustrate the innovative direction in which material science is headed, offering solutions that not only protect materials but also signal when repair is needed. These coatings incorporate indicators that change color or fluoresce in response to corrosion, providing an early warning system for maintenance. Yet, the application-specific nature of these indicators, their stability, and the reversibility of their signaling mechanisms present areas for further exploration to enhance their effectiveness and reliability. In summary, the application of micro/nanocontainers in functional coatings is a promising area of development in material science, offering smart solutions for corrosion protection and beyond. Future research will likely focus on overcoming current limitations and expanding the functional capabilities of these coatings to meet the diverse needs of various industries.

5.2. Anti-Microbial and Anti-Fouling Coatings

Regarding the development of anti-microbial and anti-fouling coatings, primarily focusing on their application in marine environments, this section highlights the challenges posed by microbial corrosion, a significant cause of deterioration in metallic structures, leading to substantial economic losses each year. The integration of anti-corrosive properties with anti-microbial and anti-fouling capabilities in coatings has shown promising potential in addressing these challenges. Recent studies have explored the encapsulation of anti-microbial and anti-fouling agents within nanocapsules to achieve active functions against microbes and fouling [84]. For instance, research by Qian [95,96] demonstrated the effectiveness of microcapsules with anti-microbial shells and anti-corrosion cores in providing both anti-microbial efficiency and self-healing properties by Pickering emulsion polymerization (Figure 16). The encapsulated agents interact with microbial cell membranes, leading to cell leakage and death, thereby exhibiting significant anti-microbial activity. Another aspect of the research focuses on biofouling, a critical concern for metal failure in seawater. Yang's study [97] on polyurethane/ZIF-8 composite coatings revealed that the anti-fouling performance of these coatings is inversely proportional to the size of ZIF-8 nanoparticles, with smaller particles showing more effectiveness. This finding indicates the potential of these coatings in significantly reducing algae adhesion compared to traditional polyurethane coatings.
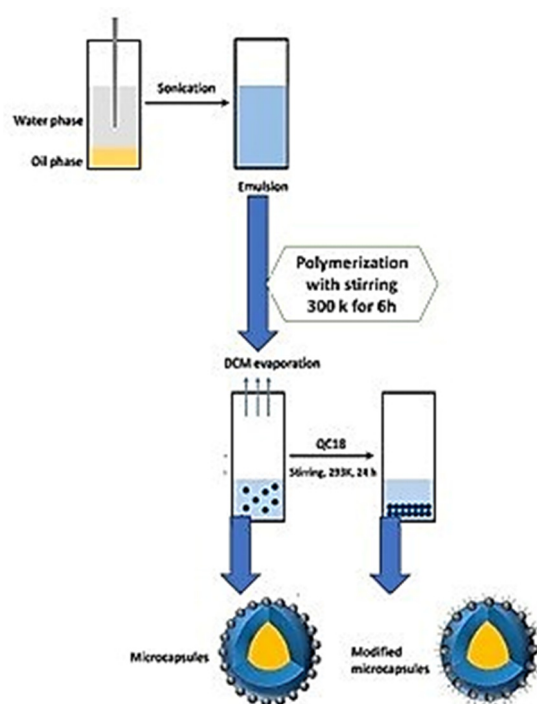
Figure 16. Outlines the synthesis of microcapsules starting with a linseed oil core, modified by a silane coupling agent, dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride, for a strong bond and durable outer layer. The schematic shows the microcapsule formation and stepwise addition of the silane agent, creating a shell that encapsulates linseed oil and adds properties like hydrophobicity or anti-microbial activity. It details the reactions and modifications at each stage, highlighting applications in self-healing coatings or controlled-release protective treatments. Reprinted/adapted with permission from Ref. [11]. 2023, Elsevier.

Additionally, the design of copolymers like the block chitosan-b-polyethylene glycol nanomicelles by Zhao [98] introduces a novel approach. These nanomicelles exhibit a reversible structure sensitive to bacterial stimulation and pH changes. The dynamic nature of these nanomicelles, which can change their charge in response to environmental conditions, demonstrates their potential in creating "non-releasing" smart anti-fouling coatings suitable

for marine applications. The trend toward environmentally friendly biological coatings is also gaining traction. Research by Barman [99] on halloysite/chitosan bio-nano composite films, which incorporate natural, renewable, and biodegradable polymers, showcases the effective use of these materials in anti-microbial applications. The controlled release of drugs from these composites makes them suitable for biomedical applications like wound healing. Similarly, Mlaeto's work [100] on bio-based anti-microbial coatings using natural phytochemical inhibitors like quercetin shows great promise in offering environmentally sustainable solutions for corrosion protection and anti-microbial applications. In summary, this section underscores the importance and effectiveness of incorporating anti-microbial and anti-fouling agents into coatings, particularly in marine environments. The advancements in nanotechnology and the shift towards eco-friendly materials are driving significant improvements in the development of coatings that are not only effective in preventing corrosion and microbial growth but also align with environmental sustainability goals.

The development and application of anti-microbial and anti-fouling coatings for marine environments mark a significant advancement in combating microbial corrosion and biofouling, which are major causes of metal deterioration. These innovative coatings integrate anti-corrosive properties with anti-microbial and anti-fouling capabilities, offering a comprehensive approach to protect metallic structures. The encapsulation of active agents within nanocapsules enables targeted release, enhancing the effectiveness of these coatings. The use of advanced materials like microcapsules with dual-function shells, ZIF-8 nanoparticles, and environmentally friendly polymers like chitosan reflects the potential of smart coatings to dynamically respond to environmental changes. Additionally, the shift towards bio-based materials emphasizes the industry's move toward environmentally sustainable solutions, reducing the ecological impact associated with traditional coatings.

However, the deployment of these coatings faces several challenges, including concerns about the environmental impact of releasing anti-microbial substances, the complexity of optimizing coating performance, and the potential increase in manufacturing costs due to the sophisticated design of these multifunctional coatings. Ensuring the long-term stability and effectiveness of these coatings in harsh marine conditions remains a critical area for further research and development. Despite these challenges, the advancements in anti-microbial and anti-fouling coatings signify a promising direction for protecting marine metal structures, aligning with sustainability goals and opening new possibilities for application in various sectors beyond marine environments. Future efforts will likely focus on addressing current limitations and expanding the scope of these innovative coatings.

5.3. Self-Lubrication Coatings

Advancements in self-lubrication coatings are increasingly vital in enhancing the reliability and extending the service life of mechanical systems. The development of such coatings is driven by the need for efficient lubrication in various manufactured products, and research in this area is gaining significant attention. Drawing inspiration from bionic designs, researchers have been focusing on creating composites with self-regulating capabilities for automatic lubrication effects. Common materials used for constructing capsule shells and porous matrices in these composites include polyetheretherketone, poly (melamine–formaldehyde), and polysulfone. These materials are chosen for their excellent formability and processability.

A notable advancement in this field was made by Guo in 2009 [101], who proposed a self-lubricating composite material based on nanocapsules. In this design, poly(melamine–formaldehyde) microcapsules, about 100 μm in size, were embedded in an epoxy resin coating. The introduction of these microcapsules resulted in a significant reduction in both the friction coefficient and wear rate of the composite material. This was attributed to the even distribution of released lubricant on the friction surface, thereby improving the tribological properties of the epoxy composite. The study also highlighted that the size of the capsules and the amount embedded significantly affect the mechanical properties of the composite materials. Moreover, researchers are exploring ways to enhance the mechanical

performance of these composite coatings. Strategies include incorporating reinforcing fillers, reducing capsule size, and enhancing interaction with the coating matrix.

In addition to their self-lubricating properties, these materials are often designed to incorporate other functionalities, making them more intelligent. For example, Yan [102] incorporated amino-functionalized $Ti_3C_2T_x$ with ZIF-8 @BTA fillers into an epoxy coating. This design enabled a pH-sensitive release of BTA inhibitors from the nanocontainers, forming a protective layer that offered both passive and active corrosion inhibition. The presence of $Ti_3C_2T_x$ at the friction interface and its high plastic deformation resistance significantly reduced the wear rate of the epoxy coating. Furthermore, common healing agents like tung oil, linseed oil, and hexamethylene diisocyanate, known for their lubricating abilities, have been successfully encapsulated into intelligent materials with self-healing capabilities. These agents are released onto the friction surface, enhancing the durability and lifespan of the coatings.

The development of intelligent self-lubrication materials with additional functionalities such as self-reporting is also highlighted. Such materials can continuously monitor lubrication status and the integrity of structures or components, enabling timely interventions to prevent material failure, thus avoiding significant losses and safety issues. Overall, the ongoing research and development in the field of self-lubrication coatings are geared toward creating more intelligent, multifunctional materials that not only improve the efficiency and longevity of mechanical systems but also contribute to safer and more sustainable industrial applications.

Self-lubrication coatings are a pivotal innovation in enhancing mechanical systems' efficiency and service life, drawing from bionic designs to create composites with automatic lubrication capabilities. Utilizing materials like polyetheretherketone and poly (melamine–formaldehyde) for their formability and processability, these coatings significantly reduce friction and wear rates, contributing to the improved tribological performance of various applications. The incorporation of nano-sized lubricant capsules within an epoxy resin matrix, as demonstrated in early research, highlights the effectiveness of these coatings in evenly distributing lubricants across friction surfaces. This innovation not only extends the durability of mechanical components but also introduces the potential for multifunctionality, including self-healing and corrosion inhibition properties, thus broadening the scope of applications for these intelligent coatings.

However, the complexity of developing these composite materials and ensuring their mechanical performance poses challenges, including the need for precise control over capsule size and distribution. Additionally, the integration of additional functionalities, such as self-reporting and enhanced lubricating agents, while promising, increases the sophistication and potentially the cost of these coatings. Despite these challenges, the shift toward self-lubrication coatings marks a significant advancement over traditional lubrication methods, offering a more sustainable and efficient solution. Future research will likely focus on optimizing these coatings' material compositions and functionalities, aiming to reduce production costs and expand their applicability across various industries, thus contributing to the development of safer and more sustainable industrial applications.

6. Conclusions

This section of the paper provides a comprehensive summary and forward-looking perspective on the field of micro/nanocontainers-based smart coatings. This paper has offered a detailed review, encompassing the synthesis or encapsulation methods of various micro/nanocontainers, the release kinetic models of encapsulated active substances, and the multifactorial triggering mechanisms for stimulus-responsive behavior. The key highlights include the successful application of micro/nano container techniques in developing smart self-healing coatings with additional functionalities such as self-reporting, anti-microbial, anti-fouling, and self-lubrication. Despite these advancements, the paper acknowledges existing challenges and areas for improvement, which are crucial for the future development of these smart coatings with enhanced corrosion resistance and multi-

functional capabilities during extended working periods. One of the primary challenges identified is the distribution and localization of micro/nanocontainers within the coating matrix. Achieving compatibility between these containers and the coating matrix without compromising the coating's physical properties or its adhesion strength to metal substrates is essential. Current studies primarily focus on the controlled release behaviors of micro/nanocontainers in isolation, but there is a need to understand these behaviors more comprehensively when the containers are embedded within the coating matrix. The review also notes that single-stimulus responsive micro/nanocontainers may be insufficient for real-world applications, where corrosion environments are often complex. Therefore, the design of multistimulus-responsive micro/nanocontainers is suggested to enhance self-healing performance and corrosion resistance under actual working conditions. Moreover, while epoxy coatings are known for their superior corrosion resistance, extending the assessment time of these coatings is necessary for a more accurate understanding of their self-healing effects. Developing materials that can repair themselves in a shorter timeframe is another key challenge, as it would significantly benefit the service life of coatings in real-world environments.

The review also emphasizes the potential of bio-inspired and environmentally friendly materials for broader application in fields such as 3D printing, biomedical materials, supercapacitors, sensors, and flexible electronic skins. These multifunctional bio-inspired self-healing coatings hold great promise for both basic research and advanced applications. Finally, the paper addresses the need to bridge the gap between laboratory research and industrial application. The main bottleneck for industrial uptake lies in developing convenient, cost-effective, and environmentally friendly methods for large-scale production of micro/nanocontainers. Systematic commercialization investigations are necessary to facilitate the industrialization of these active self-healing coatings. This transition from lab-scale to industrial-scale production remains a critical step in realizing the full potential of these innovative coatings in practical applications.

Author Contributions: Conceptualization, R.C., S.S. and D.H.O.; Data curation, S.P., S.-J.Y., K.B., S.S. and M.R.; Formal analysis, R.C., K.B., S.S., S.V., M.R. and Y.-J.J.; Funding acquisition, D.H.O.; Investigation, S.V.; Methodology, S.V., Y.-J.J., S.-J.Y. and S.P.; Software, S.V.; Supervision; D.H.O.; Roles/Writing—original draft, R.C. and S.S.; Writing—review & editing, R.C., S.S., S.V., D.H.O., S.P., K.B., M.R. and Y.-J.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by a grant from the fourth Brain Korea (BK) 21 Plus Project (Grant no. 4299990913942); Basic Science Research Program (NRF Grant no. 2021R1A6A1A03044242, 2018007551, and 2020R1A6A3A01099837); financed by the Korean Government, Republic of Korea. Researchers Supporting Project number (RSPD2023R677), Korea Basic Science Institute (Grant no. C313000); Ministry of Education, Science and Technology, Republic of Korea (2022R1F1A1063364).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: We are very grateful for the high resolution mass data provided by the Korea Basic Science Institute (KBSI, Seoul Metropolitan Center).

Conflicts of Interest: Author Simpy Sanyal was employed by the company J&L Tech and authors Ramachandran Chelliah, Su-Jung Yeon, Kaliyan Barathikannan, Selvakumar Vijayalakshmi, and Deog Hawn Oh are affiliated with Future F Biotech Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Chaouiki, A.; Chafiq, M.; Ko, Y.G. Engineering organic-inorganic frameworks as functionalized coating with remarkable active sites for boosted durability of anti-corrosion protection. *J. Environ. Chem. Eng.* **2023**, *11*, 110935. [CrossRef]
2. Manivasagam, G.; Dhinasekaran, D.; Rajamanickam, A. Biomedical implants: Corrosion and its prevention—A review. *Recent Patents Corros. Sci.* **2010**, *2*, 40–54. [CrossRef]

3. Singh, E. The Wetting of Two Dimensional Nanomaterials and Their Industrial Applications. Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, NY, USA, 2014.

4. Khairi, M.T.M.; Ibrahim, S.; Yunus, M.A.M.; Faramarzi, M.; Sean, G.P.; Pusppanathan, J.; Abid, A. Ultrasound computed tomography for material inspection: Principles, design and applications. *Measurement* **2019**, *146*, 490–523. [CrossRef]

5. Chawla, S.L. *Materials Selection for Corrosion Control*; ASM International: Detroit, MI, USA, 1993.

6. Aljibori, H.S.; Alamiery, A.; Kadhum, A.A.H. Advances in corrosion protection coatings: A comprehensive review. *Int. J. Corros. Scale. Inhib.* **2023**, *12*, 1476–1520.

7. Ahmad, S.; Habib, S.; Nawaz, M.; Shakoor, R.; Kahraman, R.; Al Tahtamouni, T.M. The role of polymeric matrices on the performance of smart self-healing coatings: A review. *J. Ind. Eng. Chem.* **2023**, *124*, 40–67. [CrossRef]

8. Purkait, M.K.; Mondal, P.; Changmai, M.; Volli, V.; Shu, C.M. *Hazards and Safety in Process Industries: Case Studies*; CRC Press: Boca Raton, FL, USA, 2021.

9. Zhang, R.; Yu, X.; Yang, Q.; Cui, G.; Li, Z. The role of graphene in anti-corrosion coatings: A review. *Constr. Build. Mater.* **2021**, *294*, 123613. [CrossRef]

10. Cao, Z.; Qin, Z.; Duns, G.J.; Huang, Z.; Chen, Y.; Wang, S.; Deng, R.; Nie, L.; Luo, X. Repair of Infected Bone Defects with Hydrogel Materials. *Polymers* **2024**, *16*, 281. [CrossRef]

11. Chen, Z.; Scharnagl, N.; Zheludkevich, M.L.; Ying, H.; Yang, W. Micro/nanocontainer-based intelligent coatings: Synthesis, performance and applications—A review. *Chem. Eng. J.* **2023**, *451*, 138582. [CrossRef]

12. Thakur, A.; Kaya, S.; Kumar, A. Recent innovations in nano container-based self-healing coatings in the construction industry. *Curr. Nanosci.* **2022**, *18*, 203–216. [CrossRef]

13. Cui, G.; Bi, Z.; Wang, S.; Liu, J.; Xing, X.; Li, Z.; Wang, B. A comprehensive review on smart anti-corrosive coatings. *Prog. Org. Coatings* **2020**, *148*, 105821. [CrossRef]

14. Zehra, S.; Mobin, M.; Aslam, R.; Bhat, S.U.I. Nanocontainers: A comprehensive review on their application in the stimuli-responsive smart functional coatings. *Prog. Org. Coatings* **2023**, *176*, 107389. [CrossRef]

15. Gong, H.; Yu, C.; Zhang, L.; Xie, G.; Guo, D.; Luo, J. Intelligent lubricating materials: A review. *Compos. Part B Eng.* **2020**, *202*, 108450. [CrossRef]

16. Yao, W.; Wu, L.; Pan, F. Self-Healing Coatings. In *Advances in Corrosion Control of Magnesium and Its Alloys*; CRC Press: Boca Raton, FL, USA, 2024; pp. 375–398.

17. Ahmadi, N.; Ramazani, A. Hybrid Magnetic Nanocatalysts for Organic Synthesis. In *Synthetic Applications*; Walter de Gruyter GmbH & Co KG.: Berlin, Germany, 2022; Volume 71.

18. Chen, S.; Huang, Z.; Yuan, M.; Huang, G.; Guo, H.; Meng, G.; Feng, Z.; Zhang, P. Trigger and response mechanisms for controlled release of corrosion inhibitors from micro/nanocontainers interpreted using endogenous and exogenous stimuli: A review. *J. Mater. Sci. Technol.* **2022**, *125*, 67–80. [CrossRef]

19. Yun, X.-W.; Tang, B.; Xiong, Z.-Y.; Wang, X.-G. Understanding self-assembly, colloidal behavior and rheological properties of graphene derivatives for high-performance supercapacitor fabrication. *Chin. J. Polym. Sci.* **2020**, *38*, 423–434. [CrossRef]

20. Aouadi, S.M.; Gu, J.; Berman, D. Self-healing ceramic coatings that operate in extreme environments: A review. *J. Vac. Sci. Technol. A* **2020**, *38*, 050802. [CrossRef]

21. Zhang, F.; Ju, P.; Pan, M.; Zhang, D.; Huang, Y.; Li, G.; Li, X. Self-healing mechanisms in smart protective coatings: A review. *Corros. Sci.* **2018**, *144*, 74–88. [CrossRef]

22. Fenker, M.; Balzer, M.; Kappl, H. Corrosion protection with hard coatings on steel: Past approaches and current research efforts. *Surf. Coat. Technol.* **2014**, *257*, 182–205. [CrossRef]

23. Tripathi, D.; Sharma, R.K.; Oztop, H.F.; Natarajan, R. *Nanomaterials and Nanoliquids: Applications in Energy and Environment*; Springer Nature: Berlin, Germany, 2023.

24. Liu, T.; Ma, L.; Wang, X.; Wang, J.; Qian, H.; Zhang, D.; Li, X. Self-healing corrosion protective coatings based on micro/nanocarriers: A review. *Corros. Commun.* **2021**, *1*, 18–25. [CrossRef]

25. Wu, Z. Design of Functional Materials for Encapsulation and Controllable Re-Lease. Ph.D. Thesis, University of Massachusetts Lowell, Lowell, MA, USA, 2021.

26. Leclercq, L.; Nardello-Rataj, V. 16 Pickering Emulsions and Biomass. In *Biorefinery: From Biomass to Chemicals and Fuels*; De Gruyter: Villeneuve d'Ascq, France, 2021; Volume 537.

27. Erol, M.; Mustafov, S.D.; Akalın, S.A.; Uzunbayır, B.; Özdemir, E.T.; Coşkun, B.; Ertekin, Z. Carbon Nanostructures for Automotive and Aerospace Applications. In *Handbook of Functionalized Carbon Nanostructures: From Synthesis Methods to Applications*; Springer International Publishing: Cham, Switzerland, 2023; pp. 1–29.

28. Huang, Z.; Shao, G.; Li, L. Micro/nano functional devices fabricated by additive manufacturing. *Prog. Mater. Sci.* **2023**, *131*, 101020. [CrossRef]

29. Christian, P. Nanomaterials: Properties, Preparation and Applications. In *Environmental and Human Health Impacts of Nanotechnology*; Wiley-Blackwell: Hoboken, NJ, USA, 2009; pp. 31–77.

30. Ouarga, A.; Lebaz, N.; Tarhini, M.; Noukrati, H.; Barroug, A.; Elaissari, A.; Ben Youcef, H. Towards smart self-healing coatings: Advances in micro/nano-encapsulation processes as carriers for anti-corrosion coatings development. *J. Mol. Liq.* **2022**, *354*, 118862. [CrossRef]

31. Chen, Y.; Wei, W.; Zhu, Y.; Luo, J.; Liu, R.; Liu, X. Synthesis of temperature/pH dualstimuli- response multicompartmental microcapsules via pickering emulsion for preprogrammable payload release. *ACS Appl. Mater. Interfaces* **2020**, *12*, 4821–4832. [CrossRef] [PubMed]

32. Xiao, Z.; Sun, P.; Liu, H.; Zhao, Q.; Niu, Y.; Zhao, D. Stimulus responsive microcapsules and their aromatic applications. *J. Control. Release* **2022**, *351*, 198–214. [CrossRef]

33. Chafiq, M.; Chaouiki, A.; Ko, Y.G. Advances in COFs for energy storage devices: Harnessing the potential of covalent organic framework materials. *Energy Storage Mater.* **2023**, *63*, 103014. [CrossRef]

34. Liang, R.-R.; Jiang, S.-Y.; Ru-Han, A.; Zhao, X. Two-dimensional covalent organic frameworks with hierarchical porosity. *Chem. Soc. Rev.* **2020**, *49*, 3920–3951. [CrossRef] [PubMed]

35. Sun, T.; Jin, K.; Wang, W.; Li, W.; Wang, T.; Yang, T.; Cheng, J.; Zhao, Z.; Chen, S. A long-term anti-corrosion and cathodic delamination resistant epoxy coating based on COF grafted GO nanofillers. *J. Ind. Eng. Chem.* **2023**, *128*, 222–234. [CrossRef]

36. Zhang, C.; Li, W.; Liu, C.; Zhang, C.; Cao, L.; Kong, D.; Wang, W.; Chen, S. Effect of covalent organic framework modified graphene oxide on anticorrosion and self-healing properties of epoxy resin coatings. *J. Colloid Interface Sci.* **2022**, *608*, 1025–1039. [CrossRef] [PubMed]

37. Qian, B.; Zheng, Z.; Liu, C.; Li, M.; D'sa, R.A.; Li, H.; Graham, M.; Michailidis, M.; Kantserev, P.; Vinokurov, V.; et al. Microcapsules prepared via pickering emulsion polymerization for multifunctional coatings. *Prog. Org. Coatings* **2020**, *147*, 105785. [CrossRef]

38. Karakuş, S.; Özeroğlu, C.; Kahyaoğlu, M.İ.; Tan, E.; İlgar, M.; Orhan, Z.; Albayrak, N. One-Dimensional Polymeric Nanocomposites-Based Microcontainers for Biomedical Applications. In *One-Dimensional Polymeric Nanocomposites*; CRC Press: Boca Raton, FL, USA, 2023; pp. 417–432.

39. Ghimire, P.P.; Jaroniec, M. Renaissance of Stöber method for synthesis of colloidal particles: New developments and opportunities. *J. Colloid Interface Sci.* **2021**, *584*, 838–865. [CrossRef]

40. Karaman, D.; Pamukçu, A.; Karakaplan, M.B.; Kocaoglu, O.; Rosenholm, J.M. Recent advances in the use of mesoporous silica nanoparticles for the diagnosis of bacterial infections. *Int. J. Nanomed.* **2021**, *16*, 6575–6591. [CrossRef]

41. Chen, Z.; Li, X.; Gong, B.; Scharnagl, N.; Zheludkevich, M.L.; Ying, H.; Yang, W. Double Stimuli-Responsive Conducting Polypyrrole Nanocapsules for Corrosion-Resistant Epoxy Coatings. *ACS Appl. Mater. Interfaces* **2022**, *15*, 2067–2076. [CrossRef]

42. Dubey, M.; Wadhwa, S.; Mathur, A.; Kumar, R. Progress in mesoporous ceria: A review on synthesis strategies and catalytic applications. *Appl. Surf. Sci. Adv.* **2022**, *12*, 100340. [CrossRef]

43. Liu, C.; Jin, Z.; Zhao, H.; Wang, L. Triple-action smart nanocontainers enhanced protective coatings with superior active and passive properties. *Prog. Org. Coatings* **2020**, *148*, 105887. [CrossRef]

44. Ma, L.; Wang, J.; Wang, Y.; Guo, X.; Wu, S.; Fu, D.; Zhang, D. Enhanced active corrosion protection coatings for aluminum alloys with two corrosion inhibitors co-incorporated in nanocontainers. *Corros. Sci.* **2022**, *208*, 110663. [CrossRef]

45. Zaitoon, A.; Luo, X.; Lim, L. Triggered and controlled release of active gaseous/volatile compounds for active packaging applications of agri-food products: A review. *Compr. Rev. Food Sci. Food Saf.* **2022**, *21*, 541–579. [CrossRef] [PubMed]

46. Kordas, G. Nanocontainers Against Biofouling and Corrosion Degradation of Materials: A Short Review With Prospects. *Front. Nanotechnol.* **2022**, *4*, 813908. [CrossRef]

47. Palo, E.; Zhang, H.; Lastusaari, M.; Salomäki, M.O. Nanometer-thick ion-selective polyelectrolyte multilayer coatings to inhibit the disintegration of inorganic upconvert-ing nanoparticles. *ACS Appl. Nano Mater.* **2020**, *3*, 6892–6898. [CrossRef]

48. Olivieri, F.; Castaldo, R.; Cocca, M.; Gentile, G.; Lavorgna, M. Mesoporous silica nanoparticles as carriers of active agents for smart anticorrosive organic coatings: A critical review. *Nanoscale* **2021**, *13*, 9091–9111. [CrossRef] [PubMed]

49. Leyva-Jiménez, F.J.; Oliver-Simancas, R.; Castangia, I.; Rodríguez-García, A.M.; Alañón, M.E. Comprehensive review of natural based hydrogels as an upcoming trend for food packing. *Food Hydrocoll.* **2023**, *135*, 108124. [CrossRef]

50. Chuhadiya, S.; Himanshu; Suthar, D.; Patel, S.; Dhaka, M. Metal organic frameworks as hybrid porous materials for energy storage and conversion devices: A review. *Coord. Chem. Rev.* **2021**, *446*, 214115. [CrossRef]

51. Shahini, M.; Mohammadloo, H.E.; Ramezanzadeh, M.; Ramezanzadeh, B. Recent innovations in synthesis/characterization of advanced nano-porous metal-organic frameworks (MOFs); current/future trends with a focus on the smart anti-corrosion features. *Mater. Chem. Phys.* **2022**, *276*, 125420. [CrossRef]

52. Wang, D.-G.; Liang, Z.; Gao, S.; Qu, C.; Zou, R. Metal-organic framework-based materials for hybrid supercapacitor application. *Co-ord. Chem. Rev.* **2020**, *404*, 213093. [CrossRef]

53. Bayer, I.S. Controlled Drug Release from Nanoengineered Polysaccharides. *Pharmaceutics* **2023**, *15*, 1364. [CrossRef] [PubMed]

54. Malekjani, N.; Jafari, S.M. Modeling the release of food bioactive ingredients from carriers/nanocarriers by the empirical, semiempirical, and mechanistic models. *Compr. Rev. Food Sci. Food Saf.* **2021**, *20*, 3–47. [CrossRef] [PubMed]

55. Liu, C.; Qian, B.; Hou, P.; Song, Z. Stimulus responsive zeolitic imidazolate framework to achieve corrosion sensing and active protecting in polymeric coatings. *ACS Appl. Mater. Interfaces* **2021**, *13*, 4429–4441. [CrossRef] [PubMed]

56. Li, H.; Qiang, Y.; Zhao, W.; Zhang, S. 2-Mercaptobenzimidazole-inbuilt metalorganic-frameworks modified graphene oxide towards intelligent and excellent anti-corrosion coating. *Corros. Sci.* **2021**, *191*, 109715. [CrossRef]

57. Su, Y.; Ojo, O.F.; Tsengam, I.K.M.; He, J.; McPherson, G.L.; John, V.T.; Valla, J.A. Thermoresponsive coatings on hollow particles with mesoporous shells serve as stimuli-responsive gates to species encapsulation and release. *Langmuir* **2018**, *34*, 14608–14616. [CrossRef] [PubMed]

58. Imanieh, A. Afshar, Corrosion protection of aluminum by smart coatings containing layered double hydroxide (LDH) nanocontainers. *J. Mater. Res. Technol.* **2019**, *8*, 3004–3023. [CrossRef]

59. Zheludkevich, M.L.; Tedim, J.; Ferreira, M.G.S. "Smart" coatings for active corrosion protection based on multi-functional micro and nanocontainers. *Electrochim. Acta* **2012**, *82*, 314–323. [CrossRef]

60. Ding, C.; Xu, J.; Tong, L.; Gong, G.; Jiang, W.; Fu, J. Design and fabrication of a novel stimulus-feedback anticorrosion coating featured by rapid self-healing functionality for the protection of magnesium alloy. *ACS Appl. Mater. Interfaces* **2017**, *9*, 21034–21047. [CrossRef]

61. Li, C.; Zhao, X.; Meng, C.; Zhang, T.; Sun, S.; Hu, S. Application of hollow mesoporous organosilica nanoparticles as pH and redox double stimuli-responsive nanocontainer in the controlled release of corrosion inhibitor molecules. *Prog. Org. Coatings* **2021**, *159*, 106437. [CrossRef]

62. Ma, L.; Wang, J.; Zhang, D.; Huang, Y.; Huang, L.; Wang, P.; Qian, H.; Li, X.; Terryn, H.A.; Mol, J.M.C. Dual-action self-healing protective coatings with photothermal responsive corrosion inhibitor nanocontainers. *Chem. Eng. J.* **2021**, *404*, 127118. [CrossRef]

63. Leal, D.A.; Riegel-Vidotti, I.C.; Ferreira, M.G.S.; Marino, C.E.B. Smart coating based on double stimuli-responsive microcapsules containing linseed oil and benzotriazole for active corrosion protection. *Corros. Sci.* **2018**, *130*, 56–63. [CrossRef]

64. Paret, N.; Trachsel, A.; Berthier, D.L.; Herrmann, A. Developing multi stimuli-responsive core/shell microcapsules to control the release of volatile compounds. *Macromol. Mater. Eng.* **2018**, *304*, 1800599. [CrossRef]

65. Xiong, W.; Tang, J.; Zhu, G.; Han, N.; Schlangen, E.; Dong, B.; Wang, X.; Xing, F. A novel capsule-based self-recovery system with a chloride ion trigger. *Sci. Rep.* **2015**, *5*, 10866. [CrossRef] [PubMed]

66. Wang, L.; Zhang, C.; Xie, H.; Sun, W.; Chen, X.; Wang, X.; Yang, Z.; Liu, G. Calcium alginate gel capsules loaded with inhibitor for corrosion protection of downhole tube in oilfields. *Corros. Sci.* **2015**, *90*, 296–304. [CrossRef]

67. Lv, L.-P.; Jiang, S.; Inan, A.; Landfester, K.; Crespy, D. Redox-responsive release of active payloads from depolymerized nanoparticles. *RSC Adv.* **2017**, *7*, 8272–8279. [CrossRef]

68. Boostani, S.; Jafari, S.M. A comprehensive review on the controlled release of encapsulated food ingredients; fundamental concepts to design and applications. *Trends Food Sci. Technol.* **2021**, *109*, 303–321. [CrossRef]

69. Fahmi, M.Z.; Prasetya, R.A.; Dzikri, M.F.; Sakti, S.C.W.; Yuliarto, B. MnFe$_2$O$_4$ nanoparticles/cellulose acetate composite nanofiber for controllable release of naproxen. *Mater. Chem. Phys.* **2020**, *250*, 123055. [CrossRef]

70. Siddiqui, S.A.; Singh, S.; Bahmid, N.A.; Mehany, T.; Shyu, D.J.H.; Assadpour, E.; Malekjani, N.; Castro-Muñoz, R.; Jafari, S.M. Release of Encapsulated Bioactive Compounds from Active Packaging/Coating Materials and Its Modeling: A Systematic Review. *Colloids Interfaces* **2023**, *7*, 25. [CrossRef]

71. Adsul, S.H.; Bagale, U.D.; Sonawane, S.H.; Subasri, R. Release rate kinetics of corrosion inhibitor loaded halloysite nanotube-based anticorrosion coatings on magnesium alloy AZ91D. *J. Magnes. Alloy.* **2021**, *9*, 202–215. [CrossRef]

72. Ghodke, S.A.; Sonawane, S.H.; Bhanvase, B.A.; Mishra, S.; Joshi, K.S. Studies on fragrance delivery from inorganic nanocontainers: Encapsulation, release and modeling studies. *J. Inst. Eng. (India) Ser. E* **2015**, *96*, 45–53. [CrossRef]

73. Ulaeto, S.B.; Rajan, R.; Pancrecious, J.K.; Rajan, T.; Pai, B. Developments in smart anticorrosive coatings with multifunctional characteristics. *Prog. Org. Coat.* **2017**, *111*, 294–314. [CrossRef]

74. Grumezescu, V.; Grumezescu, A. (Eds.) *Materials for Biomedical Engineering: Thermoset and Thermoplastic Polymers*; Elsevier: Amsterdam, The Netherlands, 2019.

75. Li, Y.; Jiang, J.; Han, S. Preparation of intelligent corrosion resistant coatings based on pH-responsive silica nanocontainers. *Microporous Mesoporous Mater.* **2023**, *349*, 112418. [CrossRef]

76. Wei, H.; Wang, Y.; Guo, J.; Shen, N.Z.; Jiang, D.; Zhang, X.; Yan, X.; Zhu, J.; Wang, Q.; Shao, L.; et al. Advanced micro/nanocapsules for self-healing smart anticorrosion coatings. *J. Mater. Chem. A* **2015**, *3*, 469–480. [CrossRef]

77. Cong, Y.; Chen, K.; Zhou, S.; Wu, L. Synthesis of pH and UV dual-responsive microcapsules with high loading capacity and their application in self-healing hydrophobic coatings. *J. Mater. Chem. A* **2015**, *3*, 19093–19099. [CrossRef]

78. Lombardo, D.; Kiselev, M.A.; Caccamo, M.T. Smart nanoparticles for drug delivery application: Development of versatile nanocarrier platforms in biotechnology and nanomedicine. *J. Nanomater.* **2019**, *2019*, e3702518. [CrossRef]

79. Altinbasak, I.; Arslan, M.; Sanyal, R.; Sanyal, A. Pyridyl disulfide-based thiol–disulfide exchange reaction: Shaping the design of redox-responsive polymeric materials. *Polym. Chem.* **2020**, *11*, 7603–7624. [CrossRef]

80. Kankala, R.K.; Zhang, H.; Liu, C.; Kanubaddi, K.R.; Lee, C.; Wang, S.; Cui, W.; Santos, H.A.; Lin, K.; Chen, A. Metal species–encapsulated mesoporous silica nanoparticles: Current advancements and latest breakthroughs. *Adv. Funct. Mater.* **2019**, *29*, 1902652. [CrossRef]

81. Ding, C.; Fu, J. Smart Anticorrosion Coatings Based on Nanocontainers. In *Smart Nanocontainers*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 413–429.

82. Sun, S.; Zhao, X.; Cheng, M.; Wang, Y.; Li, C.; Hu, S. Facile preparation of redox-responsive hollow mesoporous silica spheres for the encapsulation and controlled release of corrosion inhibitors. *Prog. Org. Coat.* **2019**, *136*, 105302. [CrossRef]

83. Tang, R.; Wang, X.; Chen, Z.; Liu, Y.; Yang, W. An S2-responsive nanocontainer for inhibiting microbial corrosion caused by sulfate-reducing bacteria. *Colloids Surf. A Physicochem. Eng. Asp.* **2023**, *663*, 131110. [CrossRef]

84. Cao, Y.; Zheng, D.; Zhang, F.; Pan, J.; Lin, C. Layered double hydroxide (LDH) for multi-functionalized corrosion protection of metals: A review. *J. Mater. Sci. Technol.* **2022**, *102*, 232–263. [CrossRef]

85. Jagtap, A.; Wagle, P.G.; Jagtiani, E.; More, A.P. Layered double hydroxides (LDHs) for coating applications. *J. Coat. Technol. Res.* **2022**, *19*, 1009–1032. [CrossRef]

86. He, X.; Chiu, C.; Esmacher, M.J.; Liang, H. Nanostructured photocatalytic coatings for corrosion protection and surface repair. *Surf. Coatings Technol.* **2013**, *237*, 320–327. [CrossRef]

87. Huang, Y.; Wang, P.; Tan, W.; Hao, W.; Ma, L.; Wang, J.; Liu, T.; Zhang, F.; Ren, C.; Liu, W.; et al. Photothermal and pH dual-responsive self-healing coating for smart corrosion protection. *J. Mater. Sci. Technol.* **2022**, *107*, 34–42. [CrossRef]

88. Li, W.; Ni, X.; Zhang, X.; Lei, Y.; Guo, J.; Jin, J.; You, B. UV-NIR dual-responsive nanocomposite coatings with healable, superhydrophobic, and contaminantresistant properties. *ACS Appl. Mater. Interfaces* **2020**, *12*, 48101–48108. [CrossRef] [PubMed]

89. Chen, T.; Chen, R.; Jin, Z.; Liu, J. Engineering hollow mesoporous silica nanocontainers with molecular switches for continuous self-healing anticorrosion coating. *J. Mater. Chem. A* **2015**, *3*, 9510–9516. [CrossRef]

90. Cheng, L.; Liu, C.; Zhao, H.; Wang, L. Photothermal-triggered shape memory coatings with active repairing and corrosion sensing properties. *J. Mater. Chem. A* **2021**, *9*, 22509–22521. [CrossRef]

91. Zadehnajar, P.; Akbari, B.; Amini, A.; Tayebi, L. Shape-Memory Polymers in Cartilage Tissue Engineering. In *Cartilage: From Biology to Biofabrication*; Springer Nature Singapore: Singapore, 2023; pp. 307–331.

92. Menon, A.V.; Madras, G.; Bose, S. The journey of self-healing and shape memory polyurethanes from bench to translational research. *Polym. Chem.* **2019**, *10*, 4370–4388. [CrossRef]

93. Li, G.L.; Möhwald, H.; Shchukin, D.G. Silica/polymer double-walled hybrid nanotubes: Synthesis and application as stimuli-responsive nanocontainers in selfhealing coatings. *ACS Nano* **2013**, *7*, 2470–2478. [CrossRef]

94. Liu, C.; Wu, H.; Qiang, Y.; Zhao, H.; Wang, L. Design of smart protective coatings with autonomous self-healing and early corrosion reporting properties. *Corros. Sci.* **2021**, *184*, 109355. [CrossRef]

95. Wang, T.; Du, J.; Ye, S.; Tan, L.; Fu, J. Triple-stimuli-responsive smart nanocontainers enhanced self-healing anticorrosion coatings for protection of aluminum alloy. *ACS Appl. Mater. Interfaces* **2019**, *11*, 4425–4438. [CrossRef] [PubMed]

96. Abu-Thabit, N.Y.; Makhlouf, A.S.H. Fundamental of Smart Coatings and Thin Films: Synthesis, Deposition Methods, and Industrial Applications. In *Advances in Smart Coatings and Thin Films for Future Industrial and Biomedical Engineering Applications*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 3–35.

97. Yang, C.; Xu, W.; Meng, X.; Shi, X.; Shao, L.; Zeng, X.; Yang, Z.; Li, S.; Liu, Y.; Xia, X. A pH-responsive hydrophilic controlled release system based on ZIF-8 for selfhealing anticorrosion application. *Chem. Eng. J.* **2021**, *415*, 128985. [CrossRef]

98. Zhao, Y.; Jiang, F.; Chen, Y.-Q.; Hu, J.-M. Coatings embedded with GO/MOFs nanocontainers having both active and passive protecting properties. *Corros. Sci.* **2020**, *168*, 108563. [CrossRef]

99. Barman, M.; Mahmood, S.; Augustine, R.; Hasan, A.; Thomas, S.; Ghosal, K. Natural halloysite nanotubes /chitosan based bio-nanocomposite for delivering norfloxacin, an anti-microbial agent in sustained release manner. *Int. J. Biol. Macromol.* **2020**, *162*, 1849–1861. [CrossRef] [PubMed]

100. Ulaeto, S.B.; Nair, A.V.; Pancrecious, J.K.; Karun, A.S.; Mathew, G.M.; Rajan, T.; Pai, B. Smart nanocontainer-based anticorrosive bio-coatings: Evaluation of quercetin for corrosion protection of aluminium alloys. *Prog. Org. Coat.* **2019**, *136*, 105276. [CrossRef]

101. Guo, Q.B.; Lau, K.T.; Zheng, B.F.; Rong, M.Z.; Zhang, M.Q. Imparting ultra-low friction and wear rate to epoxy by the incorporation of microencapsulated lubricant? *Macromol. Mater. Eng.* **2009**, *294*, 20–24. [CrossRef]

102. Yan, H.; Fan, X.; Cai, M.; Song, S.; Zhu, M. Amino-functionalized Ti3C2Tx loading ZIF-8 nanocontainer@benzotriazole as multifunctional composite filler towards self-healing epoxy coating. *J. Colloid Interface Sci.* **2021**, *602*, 131–145. [CrossRef]