

External Self-healing Coatings in Anti-corrosion Applications: A review

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ABSTRACT

Nowadays corrosion has become an urgent problem to be solved. Scientists are committed to finding various ways to restrain the corrosion of metals. The anti-corrosion coating is considered to be an economical and effective method. However, the conventional anti-corrosion coating is vulnerable to be damaged. The external self-healing coating can release the active healing agent when destroyed and prevent the corrosion spontaneously, which has been the subject of increasing interest. In this paper, the anti-corrosion application of external self-healing coatings was described in detail, including organic micro/nano container-based, inorganic micro/nano container-based and microvascular network-based self-healing coatings. First, the present article introduced the development, preparation and self-healing properties of the external self-healing coating. In the successive chapter, the anti-corrosion performance of the coating was highlighted. Besides, some open problems and future challenges were also investigated. Finally, special attention was dedicated to the prospect of the external self-healing coating. This review provides readers with an overview of achievements to date and insights into the future development of engineering applications to promote the large-scale application of external self-healing anti-corrosion coatings.

INTRODUCTION

Corrosion poses a substantial economic burden and even leads to catastrophic accidents.¹⁻³ In order to prevent or slow down the corrosion kinetics, corrosion inhibitor, cathodic protection, and coating

barrier protection are commonly used.⁴⁻⁶ Adding corrosion inhibitors directly in the corrosive environment is a common method to suppress metal corrosion. However, it is difficult to control the effective release of corrosion inhibitors and eventually leads to unnecessary waste. Cathodic protection is also an effective electrochemical protection method, which includes two forms of impressed current and sacrificial anode. The principle of cathodic protection is to reduce the natural corrosion potential of the protected structure to a non-corrosion level. The sacrificial anode cathodic protection connects the metal with a more negative potential to the protected metal, so that electrons on the metal are transferred to the protected metal, and the entire protected metal is at a relatively negative potential, thereby reducing the metal corrosion rate. However, the anode has a limited operating life as well as requiring regular replacement, which is economically unsuitable for protecting large and poorly coated pipes. While the external current cathodic protection can flexibly control the output of the current and has wider applicability. It brings a large number of electrons to the metal by adding a direct-current power supply and an auxiliary anode, making the potential of the protected metal lower than the surrounding environment, thus the metal oxidation reaction is suppressed. But this undoubtedly increases installation and maintenance costs.⁷⁻⁹ Covering metal surfaces with an anti-corrosion coating is a more economical and reliable method. The coating can effectively block the direct contact between corrosive ions and the metal substrate, hence inhibiting the occurrence of corrosion. However, in the process of use, traditional passive coatings are often subject to mechanical damage and cause the anticorrosive coating to crack, making its anticorrosive effect weaken or even fail.^{10, 11} People usually judge the coating damage location by electrochemical means and then perform manual repair, which increases the consumption of manpower and material resources. As a kind of intelligent protective coating, the self-healing coating not only has the passive barrier function of traditional coatings but also develops an active protection function, attracting much academic attention.^{12, 13}

The self-healing material was first put forward in the 1980s and it is still a research hotspot to date.¹⁴⁻¹⁶ According to whether the coating is implanted with an external repair agent, the self-healing coating can be divided into two types: intrinsic and external. The intrinsic self-healing coating does not require the implantation of an external repair agent, because the coating itself contains a specific molecular structure. Under the external stimulus, the original function and structure of the coating are restored through reversible reactions, such as the Diels-Alder reaction,^{17, 18} hydrogen bonding reaction¹⁹ and disulfide bonding reaction.^{20, 21} Although the intrinsic self-healing coating can perform multiple cycles of self-healing, the realization of reversible reactions is limited by specific functional groups, so it is difficult to be widely used in industrial production.^{22, 23} On the contrary, the external self-healing coating can release the carried healing agent and fill the damaged area of the coating, so as to achieve self-repair.²⁴ Originally, inorganic substances, such as chromate, were directly doped in the coating.^{25, 26} However, these inorganic corrosion inhibitor ions are toxic, so the leakage of corrosion inhibitor will cause serious environmental pollution. Therefore, scientists began to look for a variety of environmentally friendly organic corrosion inhibitors.²⁷⁻²⁹ However, the direct contact between the repairing agent and the coating substrate will produce an adverse chemical reaction, which may affect the performance of the repairing agent and the coating. So people consider encapsulating the repair agent in microcapsules,³⁰⁻³² hollow fibers^{33, 34}, and microvascular networks.^{35, 36} When the local environment changes, the micro/nano container responds to external signals, releases the encapsulated active material, and actively repairs the structure and performance of the coating. This method avoids the premature leakage of the repair agent, selectively repairs the damaged

area of the coating, and greatly improves the overall performance and service life of the coating.

Research on self-healing coatings has grown rapidly in recent years, as evidenced by a large number of published patents,³⁷⁻⁴⁵ books,⁴⁶⁻⁵⁰ and articles.⁵¹⁻⁵⁶ Compared to the intrinsic self-healing coating, the external self-healing coating is more likely to be commercialized in the near future, due to its abundant raw materials and mature processes. However, there are few reports on review articles of the external self-healing anti-corrosion coating. To this end, this review systematically reports the latest developments in this research area. The self-healing coating through reversible reactions is not the focus of this article, and the related content can refer to the recently published review.⁵⁶ Compared with recent reviews focusing only on microcapsules,⁵⁷⁻⁵⁹ this review provides a comprehensive discussion on the preparation, self-healing properties and anti-corrosion mechanisms of the organic micro/nano container-based, inorganic micro/nano container-based and microvascular network-based self-healing coatings.

THE EXTERNAL SELF-HEALING COATING

The organic micro/nano container-based self-healing coating

The mechanical action was first used to test the performance of self-repairing microcapsules, which is a common coating damage mode. Kolmakov et al.⁶⁰ utilized a computational model to design a mechanically responsive microcapsule, which responds to mechanical deformation through shape changes and releasing the carried nanoparticles. The pH-responsive capsule is more suitable for self-healing anti-corrosion coatings, which is the focus after the mechanical action. When corrosion occurs on the metal surface, the pH in the surrounding environment decreases with anodic dissolution while increases with cathodic reaction. Then the active agent released from the microcapsule, preventing the corrosion process. Besides, the light, temperature, magnetic field, etc. are also common external stimuli.^{61, 62} Chen et al.⁶³ synthesized an ultraviolet (UV) response capsule with titanium dioxide and silica nanoparticles as pickling agents, by pickling emulsion polymerization, then dispersed them into the aqueous polysiloxane. Because of the photochemical reaction, the structure of the capsule changed and the healing agent was released after absorbing the UV light. Leal et al.⁶⁴ prepared a multi-responsive microcapsule containing linseed oil (LO) and benzotriazole (BTA) by in situ polymerization. The BTA was encapsulated between the polyelectrolyte layers of microcapsules by layer-by-layer (LbL) polymerization. When the coating was mechanically damaged, the LO in the capsule will be released, inhibiting the occurrence of corrosion. At the same time, the BTA would be released from the polyelectrolyte layer and adhered to the surface of the metal substrate when the pH value decreased, which impeded the occurrence of corrosion.

The preparation of microcapsules is mainly achieved by physical methods, chemical methods, and physicochemical methods, of which in situ polymerization and interfacial polymerization are the most common methods. The in-situ polymerization method is to disperse the monomer and catalyst in the dispersed phase or continuous phase. The monomer reacts chemically under the action of the catalyst to produce a poorly soluble polymer, which coats the core material to form microcapsules gradually. And the size of the microcapsules can be controlled by changing the stirring rate so that it is easy to industrialize.⁶⁵ The principle of the interfacial polymerization is to form microcapsules by polymerization reaction between the core material in the dispersed phase and the monomer in the continuous phase. The

process is simple and the reaction speed is fast, but the reactive monomer is required to carry out polycondensation reactions.⁶⁶ In this section, the preparation and healing mechanism of the organic micro/nano container-based self-healing coating are expounded in detail, according to the type of healing agent.

The corrosion inhibitor-based self-healing coating

For the corrosion inhibitor-based self-healing coating, the inhibitor is encapsulated in the polymer capsule. When the coating is stimulated by mechanical action, light, temperature, and other external stimuli, the corrosion inhibitor will be released from the capsule and penetrated the cracks of the coating. So the anodic dissolution and cathodic reaction on the surface of the metal substrate are restrained, which alleviates the corrosion rate,⁶⁷ as shown in Figure 1. The BTA,⁶⁸ mercaptobenzothiazole (MBT)⁶⁹ and imidazole⁷⁰ are used as organic corrosion inhibitors at present. And the anti-corrosion mechanism of organic corrosion inhibitor is divided into two steps. First of all, the corrosion inhibitor is transferred on the surface of the corrosive metal substrate. Then, the inhibitor molecules interact with the metal surface through physical and chemical adsorption to form a protective film on the surface of the metal substrate, hindering the occurrence of corrosion. The popular inorganic corrosion inhibitors mainly include phosphate, silicate, nitrite and so on.⁷¹⁻⁷³ These inorganic salts combine with metal cations in the anode region to form a passivation film on the surface of the metal substrate, which inhibits the corrosion of the metal substrate.

Tavandashji et al.⁷⁵ prepared a hollow nano-polyaniline capsule encapsulating MBT corrosion inhibitor by the soft template method. When the pH value of the coating defect increased at the initial stage of corrosion, the corrosion inhibitor was released from the capsule to prevent corrosion. The results of electrochemical impedance spectroscopy (EIS) and scanning vibrating electrode technology (SVET) indicated that the coating encapsulated with corrosion inhibitor was more anticorrosive than the pure epoxy coating. Choi et al. stored triethanolamine (TEA) in modified hollow latex nano-capsules. In an acidic or alkaline environment, the TEA was rapidly released from the capsules to inhibit the corrosion of cold-rolled steel.⁷⁶ Some scholars also consider using the LBL to inlay the corrosion inhibitor on the surface of capsules to improve the protective performance of the coating. Modified polyvinyl alcohol (PVA) microcapsule was produced by Shi and his teammates.⁷⁷ The polyethylene imine (PEI), sodium polystyrene sulfonate (PSS) and BTA were loaded on the surface of the microcapsule by the LbL technique. When the local pH changed by the corrosion of the material matrix, the BTA would be released, thus preventing the further occurrence of corrosion. This way improves the protective function of the coating to the substrate obviously and is suitable for the self-repair of large cracks, while it has not been popularized and applied until now. The corrosion inhibitor was embedded on the surface of the capsule because there are many disadvantages in directly encapsulating the corrosion inhibitor together with the active body in the capsule. First, stability and compatibility problems may be caused if the corrosion inhibitor and the active body are packaged together, and both are likely to have a chemical reaction, thereby affecting the self-healing effect. In addition, the active agent in the capsule is viscous generally, which makes the corrosion inhibitor outflow difficultly, and cannot achieve self-heal efficiently. How to release corrosion inhibitor accurately and effectively is the main problem of microcapsules. Abbaspourrad et al.⁷⁸ reported a microfluidic method to produce monodisperse pH-responsive microcapsules with accurate controlled release characteristics. By controlling the thickness of the capsule shell, the amount of time needed to completely dissolve the shell is controlled,

so as to control the final release time of the corrosion inhibitor in the microcapsule. The permeability of the shell can be controlled independently, and the speed of each microcapsule releasing its inhibitor can be controlled by changing the proportion of pH response polymer in the microcapsule shell. Besides, the trigger value of pH can be controlled by changing the composition of microcapsules and using acid-sensitive or alkali-sensitive microcapsules. Therefore, the corrosion inhibitor in microcapsules can only be released at a specified rate under a specified time delay and ideal pH value.

Except for the pH-responsive self-healing coating, the redox-responsive self-healing coating is much reported. Using the interface of microemulsion droplets as a soft template, Lv et al.⁷⁹ designed a kind of redox nano-capsules composed of conductive polyaniline and polypyrrole shell by oxidative polymerization, which encapsulated hydrophobic corrosion inhibitor. The results of the scanning electron microscope (SEM), transmission electron microscope (TEM) and cyclic voltammetry showed that the corrosion inhibitor can be released quickly under the condition of reduction and slowly under the condition of oxidation, so it has a good prospect of anticorrosive application. Vimalanandan et al.⁸⁰ prepared conductive polymer (CP) based nano-capsules by micro-emulsion synthesis method, using redox responsive polyaniline (PANI) and 3-nitrosalicylic acid (3-NISA) as shells and corrosion inhibitors, respectively. Gold nanoparticles (AuNPs) were decorated on the surface of the capsule to avoid direct contact between metal and CP. During the reduction process, the addition of cations to the polymer resulted in an increase in the volume of the capsule and permeability of the shell, then the inhibitor was released. The effective release of corrosion inhibitors is the key to realize the self-healing performance of the coating. Lv et al.⁸¹ used the organic sulfur 2, 5-dimercapto-1, 3, 4-thiadiazole (DMcT) as the corrosion inhibitor, realizing the series oxidative polymerization of aniline and DMcT in microemulsion droplets. The thiol group at both ends of the DMcT molecule can be combined to form a poly 2,5-dimercapto-1,3,4-thiadiazole (PDMcT) polymer, and depolymerized into a DMcT monomer after reduction, which avoided the unnecessary release of DMcT when the capsule is not activated.

Mutual adaptation of the corrosion inhibitor and the capsule is the key to improve the self-healing performance of the coating. For the inhibitor carrier, we hope that it has enough load capacity, and can release the inhibitor accurately as needed. For the corrosion inhibitor itself, the appropriate corrosion inhibitor should be selected according to the properties of the material. The agent encapsulated in the capsule can be a single corrosion inhibitor or a combination of multiple corrosion inhibitors. However, capsules coated with corrosion inhibitors only impede corrosion of the material substrate, while having weak protective properties.

The healing agent-based self-healing coating

Unlike the corrosion inhibitor-based self-healing coating, the healing agent-based self-healing coating uses epoxy resin, dicyclopentadiene (DCPD), and vegetable oil as repair agents. Under the stimulation of the external environment, these repairing agents are released. Then the polymerization reaction takes place to form a cross-linked structure to bond the cracks, thus realizing self-healing.^{55, 82} Normally, the size of healing capsules is often larger than that of corrosion inhibitor capsules. On one hand, in order to prevent the passage of external corrosive components (oxygen and water), a large number of healing agents are needed to fill the damaged area of the matrix physically. And it is necessary to increase the load capacity of the capsules by increasing the size of the capsules when the number of capsules is determined. On the other hand, a sufficient healing agent completely covers the exposed areas of the metal substrate to achieve

good corrosion resistance, while a relatively small amount of corrosion inhibitor can prevent corrosion.

White et al.³⁰ manufactured a polyurea formaldehyde (PUF) self-healing microcapsule encapsulating DCPD monomer healing agent by in situ polymerization firstly. The microcapsule and powdered Grubbs catalysts were dispersed in the epoxy resin matrix. However, the prepared microcapsules are not suitable for coatings, due to the huge microcapsules, between 100-180 μm . Such giant microcapsules would disrupt the barrier effect with the microcapsule-doped coating. Therefore, it is necessary to prepare sub-micron and even nano-scale uniform capsules. Sun et al.⁸³ prepared DCPD@PF nanocapsules by hydrothermal synthesis and liquid phase switching transport technology, taking the DCPD as core material and phenol formaldehyde (PF) as shell material, as shown in Figure 2. The synthesized DCDP@PF nanocapsules have a diameter of about 500 nm and a shell thickness of about 50 nm. After adding 15 wt.% DCPD@PF capsules to the epoxy resin matrix, the fracture toughness of the coating was increased by 81.4%, the tensile strength was increased by 26.6%, and the fracture toughness recovery rate was 91.8%. The addition of the capsule not only effectively improves the mechanical properties of the coating, but also makes the coating have efficient self-healing properties.

In order to re-bond the crack interface, the healing agent from the ruptured capsule should preferably have a chemical composition and mechanical strength matched with the anticorrosive coating and the metal. In this sense, epoxy resin can be considered an excellent choice, because of its superior adhesion and strength.^{84, 85} Using the epoxy resin as the repair agent, Yuan et al.⁸⁶ successfully prepared PUF microcapsules by in situ polymerization, with an average diameter of 145 μm . The capsule can be stored stably at room temperature and the chemical properties of the capsule remain stable as long as the heating temperature does not exceed 238°C. Based on the study of Yuan, Yang et al.⁸⁷ produced a PUF microcapsule with an average diameter of 100 μm . And the capsule also has good stability at room temperature as well as high-temperature resistance. Yan et al.⁸⁸ prepared urea-formaldehyde (UF) microcapsules by in-situ polymerization, taking the epoxy resin as core material. The microcapsules were dispersed in waterborne wood coatings to explore the effect of microcapsules on the properties of waterborne wood coatings. The result revealed that when the microcapsule concentration is 10 wt.%, the waterborne wood coating has the best comprehensive properties, such as gloss, hardness, adhesion and impact resistance.

For the catalyst-dependent healing agent mentioned above, the realization of self-healing requires the participation of a catalyst, which reacts with the healing agent to solidify the healing agent on the metal surface. However, when the catalyst fails, the defects cannot be filled, resulting in the loss of the protective function, which greatly limits the scope and further development of self-healing coatings. At the same time, the release ratio of the healing agent and the catalyst cannot be controlled, material waste may occur and the desired curing effect may not be achieved. In addition, the catalyst is expensive, which increases the production cost of the coating. Therefore, the realization of self-healing through catalyst-free and single-response therapy has attracted more attention.

The vegetable oil is economical and environmentally friendly, and it is no need for additional catalyst in the self-heal process, attracting increasing attention. At present, the vegetable oil used in self-healing coating mainly includes dry oil and some semi-dry oil. Dry oil can be used as an oxidizing healing agent to react with oxygen to solidify the oil. It covers the metal surface and blocks corrosive substances from contacting the metal substrate to inhibit corrosion. The LO and tung oil

(TO) are the most widely used drying oils.⁸⁹⁻⁹¹ In 2008, Suryanarayana et al.⁹² used linseed oil as a repairing agent and prepared microcapsules with excellent properties by urea-formaldehyde polymerization. When the coating was destroyed, the LO released from the microcapsule and the matrix crack was repaired successfully. Behzadnasab et al.⁹³ created linseed oil-filled urea-formaldehyde microcapsules with different particle sizes (0-300 μm) by in situ polymerization. The experimental results show that the corrosion resistance is the strongest when the mass fraction of the microcapsule is 10%. And the effect of microcapsule size on corrosion resistance is more significant than that of loading concentration. In the 0-300 μm particle size range, larger microcapsules are more likely to break during the scratch process and lead to better self-healing. In addition, results from EIS indicated that although flaxseed oil can significantly improve the corrosion performance of the damaged coating in a short time, the corrosion performance of LO would decrease rapidly with the passage of time. This may be due to the penetration of water and ions into the newly formed LO layer, resulting in a decrease of corrosion resistance of the coating. The TO has similar properties to linseed oil. It can be polymerized into a hard-solid film to fill the coating defects and restore the barrier properties of the coating. Urea-formaldehyde microcapsules encapsulated with TO were prepared through in-situ polymerization by Samadzadeh et al.⁹⁴ compared to pure epoxy coatings, the TO microcapsules coatings have better corrosion resistance. Taking the TO as the core material, Fayyad et al.⁹⁵ prepared three urea-formaldehyde microcapsules with different sizes (88 μm , 200 μm , 250 μm) by in-situ polymerization. The effect of TO microcapsule size on the self-healing and anticorrosive properties of the coating was studied. The results show that compared with the coating with larger microcapsules, the coating with smaller microcapsules has higher corrosion resistance, lower roughness, and better self-healing performance.

The soybean oil (SBO) also has been considered versatile due to its economy and availability. Unlike dry oils such as LO and TO, the soybean oil is a semi-drying oil that is slow to dry and often requires the additional desiccant to increase the drying rate. Shisode et al.⁹⁶ wrapped the cobalt desiccant and soybean oil in urea-formaldehyde (UF) microcapsules. With 0.5 wt.% cobalt, the soybean oil could be quickly oxidized and dried, which improved the corrosion resistance of the substrate. More recently, regarding the epoxy soybean oil (ESO) as main raw material, hexamethylene Diisocyanate (HDI) and *o*-cresyl glycidyl ether (CGE) as reaction diluents, Yang et al.⁹⁷ manufactured a kind of PUF microcapsules by in situ polymerization of water in oil emulsion. The microcapsules were dispersed in the epoxy coating uniformly, as shown in Figure 3. When the coating is mechanically damaged, the released core material quickly undergoes photopolymerization under sunlight, covering the damaged area and inhibiting the corrosion. In addition, the presence of micro/nano-scale structures like lotus leaves on the surface of the microcapsules enables the coating to have superhydrophobic properties, which prevents corrosive liquids from penetrating into the coating. Therefore, the epoxy coating embedded in the microcapsules not only has excellent self-repairing performance, but also has the ability of self-cleaning, showing outstanding anti-corrosion performance.

The inorganic micro/nano container-based self-healing coating

Organic microcapsule self-healing coatings are inevitably unable to reach certain areas of the coating, due to the uneven dispersion of the capsules. At the same time, compared with inorganic nanocontainers, the preparation process of organic microcapsules is complex. Inorganic nanocontainers have a wider range of structures and properties than ordinary capsules and are considered to be the

most likely substitute for organic capsules.⁹⁸ At present, the commonly used inorganic nanocontainers include halloysite (HNT), mesoporous silica, layered hydroxide (LDH) and so on. And they all have the characteristics of large storage space and dispersed structure.

The HNT has a natural nanotube-like structure, which is mainly composed of silicate and has good biocompatibility.⁹⁹⁻¹⁰¹ Under the same load capacity, it shows excellent aerodynamic, hydrodynamic performance, and better processing ability than spherical microcapsules.¹⁰²⁻¹⁰⁴ In 2008, Lvov et al.¹⁰⁵ first reported a natural HNT nanotube that can be used to store and release repair agents sustainably for dozens of days, making a significant contribution to the development of HNT-based nanocontainers. Fix et al.¹⁰⁶ embedded the HNT nanotubes carrying corrosion inhibitors in a sol-gel matrix, to study the anti-corrosion properties for aluminum AA2024. The SVET test shows that, for pure sol-gel coatings and sol-gel coatings of HNT nanotubes without corrosion inhibitors, the maximum current density increases with corrosion time. For sol-gel coatings of HNT nanotubes containing corrosion inhibitors, the maximum anode activity decreases rapidly within 1-2 hours, which indicates that the release of the corrosion inhibitors achieves self-healing of the coating. Abdullayev¹⁰⁷ further controlled the release of corrosion inhibitors and formed blockers at the end of the tube through the interaction of BTA loaded in the tube with a massive copper ion solution. By controlling the strength of the scale inhibitor complex, the adjustable release of BTA can be realized and the release time can reach hundreds of hours. Sun et al.¹⁰⁸ added HNT and BTA-loaded HNT (BTA-HNT) to silicate electrolytes respectively, to prepare plasma electrolytic oxidation (PEO) coatings on AM50 alloys. The corrosion behavior of coatings in 3.5 wt.% NaCl was investigated by EIS and plasma display panel (PDP) scanning. The results show that the addition of HNT enhances the scratch resistance and bond strength of the coating. Both the PEO and HNT-PEO coatings showed a tendency of pitting corrosion, while the BTA-HNT-PEO coatings mainly exhibited uniform corrosion and good corrosion resistance. Because of the self-healing function of the BTA-HNT-PEO coating, pitting corrosion was suppressed. Like MBT, the L-Val is a commonly used green corrosion inhibitor. Due to its proper isoelectric point spacing, it can be adsorbed on HNTs by electrostatic force. Dong et al.¹⁰⁹ loaded L-Val and MBT into HNTs, preparing two types of pH-responsive anticorrosive materials. The results show that both types can achieve the controlled release of the inhibitor and the self-healing performance of the coating, but the ability of HNTs to carry L-Val is higher than MBT, which are 12% and 7%, respectively. When the pH is 10, 98% of the adsorbed L-Val molecules are released from HNTs within 300 min, while MBT needs to be released for 120 h to reach the same ratio. According to the EIS experiment, it can be concluded that the anticorrosive performance of L-Val-loaded HNTs is better than MBT-loaded HNTs. Therefore, when coating defects occur, L-Val-loaded HNTs provide faster self-healing ability and excellent corrosion resistance.

Compared with HNTs, the mesoporous silica has a larger pore volume and specific surface area. It can not only control the release of corrosion inhibitor preferably but also improve the toughness and barrier properties of the coating substrate.¹¹⁰⁻¹¹² Borisova et al.¹¹³ embedded monodisperse mesoporous silica nanoparticles loaded with BTA into SiO_x/ZrO_x sol-gel coating to study its self-healing and anticorrosive properties for aluminum alloy. The mesoporous silica has good mechanical stability, which can effectively plug the area of micropores, cracks and low cross-linking density in passivated SiO_x/ZrO_x coating, and improve its physical barrier performance. When the local pH of the metal substrate changed, the BTA was released from the nano-container to achieve active self-repair. This study provided a basis for the superior performance of mesoporous silica nanocontainers and their role in improving the performance of active

anti-corrosive coatings. Borisova et al. also studied the effects of the size,¹¹⁴ concentration¹¹⁵ and position¹¹⁶ of mesoporous silica on the self-healing properties. The result revealed that the coating with small particle size was better than that of a large size. The concentration of the mesoporous silica nano-container should be controlled at about 0.7%. Otherwise, the improper concentration will affect the corrosion resistance of the coating. Increasing the distance between the metal surface and the nanocontainer results in better barrier properties, while results in worse active corrosion inhibition performance. Saremi et al.¹¹⁷ used mesoporous silica nanovessels as the smart body of molybdate corrosion inhibitors for polypyrrole coatings. The results show that the release amount of corrosion inhibitor is larger in the medium with higher pH value and greater chloride ion attack. The presence of a corrosion inhibitor in mesoporous silica protects the steel better than a coating without a corrosion inhibitor. Unlike traditional inhibitor loading methods for mesoporous silica nanoparticles, Xu et al.¹¹⁸ proposed a simple one-step method for preparing BTA-loaded mesoporous silica nanocontainers without additional steps, such as template removal or inhibitor loading, as shown in Figure 4. The prepared nanocontainer has a high corrosion inhibitor loading (~16 wt.%) and has H⁺ ion reactive corrosion inhibitor release characteristics. When the pH is changed by the anode reaction on the surface of the metal substrate, the BTA corrosion inhibitor is released with the dissolution of the cetyltrimethylammonium bromide (CTAB) micelles, and it diffuses to the active parts of the anode or cathode, to inhibit corrosion in time. Maia et al.¹¹⁹ prepared a smart nanoreservoir for the first time in a one-step method, using silica nanocontainer (SiNC) as a carrier and MBT as a corrosion inhibitor. Unlike traditional mesoporous silica nanoparticles, SiNC has a hollow core and shell with progressive mesopores, which gives a significant load capacity. Under the condition of acidic pH and high concentration of NaCl, SiNC can slowly release a large amount of MBT for a long time. So it can be used in anti-corrosive systems that require a long-term release.

The LDH is a typical anion exchange material consisting of a stack of positively charged mixed metal hydroxides, with anionic and solvent molecules interposed therebetween, which has a unique layered structure, ion exchangeability, and adsorption. It can be used as a corrosion inhibitor to exchange corrosive anions in a corrosive environment to achieve the release of corrosion inhibitors. Because of its low toxicity, biocompatibility and controllable release of active additives, LDH has been widely used in the field of metal corrosion.¹²⁰⁻¹²² Zheludkevich et al.¹²³ prepared Mg/Al and Zn/Al LDH-nanocontainers by direct synthesis and anion exchange method. The release kinetics of bisvanadate anions (VO₃⁻) carried between nanocontainer layers was studied. In 0.05 M NaCl solution, compared with the directly synthesized Zn₂AlVO₃ LDH, the ion exchange performance of Zn₂AlVO₃ LDHs prepared by anion exchange method was significantly improved. Although the concentration of vanadate anions released by Mg₂AlVO₃ LDH prepared by direct synthesis is the highest, due to the dissolution of some of the magnesium salts, the Mg²⁺ concentration in the solution is higher, which may affect the anion exchange performance. In addition, the anion exchange reaction is chemical, and the concentration of vanadate in the solution is controlled by the ion exchange balance rather than the solubility balance. Wang et al.¹²⁴ successfully prepared benzoate-LDHs (BZ-LDHs) composites by co-precipitation method. The release kinetics of benzoate anion in the LDHs matrix was studied. In 3.5 wt.% NaCl solution, chloride ion exchanges with benzoate anion, benzoate anion is slowly released, the chloride ion is adsorbed by LDHs, and the chloride ion concentration in the solution decreases continuously (Figure 5 (a), (b)). Since the ion exchange process is an equilibrium process, the ion exchange rate is less than 100%, that is, the benzoate anions in the LDHs matrix cannot be completely exchanged. XRD

(Figure 5 (c)) and FT-IR (Figure 5 (d)) were used to analyze the 3.5 wt.% NaCl solution containing BZ-LDHs after the release test, which also explained the above release mechanism of the BZ-LDHs system. Yasakau et al.¹²⁵ studied the corrosion resistance of a two-layer sandwich system consisting of a sol-gel coated LDH conversion layer. The surface cleaning process of AA2024, the type of negative ions in LDH structure and the influence of the presence of the sol-gel film on the active corrosion resistance of the bilayer system were discussed in detail. What is more, the type of metal ions will also affect the structure of LDHs and the corrosion performance of the system. Taking vanadate as a corrosion inhibitor, Liu et al.¹²⁶ applied nickel-based LDHs and zinc-based LDHs sealing layers to anodic aluminum oxide film (AAO) to study its corrosion resistance to aluminum alloy. Compared with the zinc-based LDH, the nickel-based LDH has smaller sheet size, larger surface area and higher density, which can carry more corrosion inhibitors. The EIS result shows that the impedance value of nickel-based LDHs outer layer decreased from $5.438 \times 10^4 \Omega \text{ cm}^2$ to $9.035 \times 10^3 \Omega \text{ cm}^2$, while that of zinc-based LDHs outer layer decreased from $2.864 \times 10^4 \Omega \text{ cm}^2$ to $5.235 \times 10^3 \Omega \text{ cm}^2$ after immersion in 3.5 wt.% NaCl solution for 14 days. Therefore, nickel-based LDHs as a sealing layer has better anti-corrosion performance for aluminum alloy. In addition, the graphene oxide (GO) and its composites have been widely used in inorganic nano-containers because of their excellent barrier properties and good dispersion properties. Based on the electrostatic interaction between negatively charged graphene oxide (GO) and positively charged phosphoric acid intercalated hydroxycalcite (PIH), Chen et al.¹²⁷ obtained GO@PIH hybrid products by electrostatic self-assembly method and applied them to waterborne epoxy resin coatings (WECs). The epoxy coating sealed with GO@PIH hybrid products showed better corrosion resistance and barrier performance compared with the common waterborne epoxy coating. It is worth noting that, like LDH nanocontainers, GO@PIH based epoxy coatings also achieve storage and release of corrosion inhibitors by electrostatic adsorption.

The microvascular-based self-healing coating

The repair agents carried by micro/nano containers are limited, so it is difficult to repair multiple times in the same place. Therefore, micro/nano containers are only suitable for self-repair of small cracks, but not for large-scale wear damage. However, this problem does not exist in the microvascular self-healing coating because of its large loading capacity. The microvascular structure is similar to the vascular network of the organism where the capillary or hollow fiber is interdigitated in the matrix material and extended to various parts of the coating. When the coating is subjected to external mechanical shock, the microvascular channel is broken, and the released repair agent supplies the crack continuously to restrain the corrosion process. In theory, cracks in any direction can be repaired, and multiply damaged sites can be repaired cyclically.^{35, 128} The electrospinning and solution blowing are common methods for the preparation of hollow fiber structures. The vascular network prepared by electrospinning has good slow release and controllability for self-healing agent which is loved by people.^{129, 130} Figure 6 shows the principle of preparation by the electrospinning method. The coaxial electrospinning is a simple and reliable technique for encapsulating liquid healing agents in nano vascular structures. It only requires that the shell material is a spinnable viscoelastic polymer and there is no requirement for healing agent.^{131, 132} The emulsion electrospinning is a more convenient method of electrospinning. It requires only a simple single-outlet needle and does not require a coaxial needle. This makes it easier to control the jet of a single-outlet needle, but the requirement of the core material is very strict. Nanofibers prepared by solution blowing method have better quality and faster output compared with electrospinning, which is suitable for industrial large-scale production. Nanofibers prepared by solution blowing method often contain a large

number of healing agents. The more the number of healing agents, the more likely the healing agent to release and heal the damaged area, and the better the self-repair effect.^{133, 134}

As early as the end of the 20th century, people began to study the self-healing performance of the hollow tube.¹³⁷ Dry et al. introduced the repair effect of a hollow glass pipe on cement concrete cracks firstly.¹³⁸ The result showed that the structural properties of the matrix material were improved and the self-healing function of the crack was also realized. The hollow glass tube had become the earliest hollow fiber self-healing material. Besides, scientists began to research on hollow glass fibers and hollow polymer fibers. Trask et al.¹³⁹ realized the bionic self-repair of epoxy resin coating by using fiber reinforced composite (FRPs). Result meant that the initial strength of the matrix was reduced by 16% with the addition of hollow glass fiber. The FRP laminate with a hollow fiber layer healed successfully and the strong recovery rate was 87%. In recent years, scientists have begun to focus on nanoscale self-healing hollow fibers. Compared with the micron scale, the nanometer hollow fiber has a smaller size and better compatibility with the coating substrate, which can be used in thinner coatings. Dong et al. prepared polyvinyl alcohol/polyvinylidene fluoride core-shell nanofibers by coaxial electrospinning.¹²⁹ The structure of the nanofiber was uniform when the feed speed of the shell was controlled at 1.5 mL/h. And if the shell feed rate was too slow or too fast, the nanofiber diameter would be uneven. The EIS indicated that the coaxial nanofibers loaded with MBT improved the barrier performance and corrosion resistance of the coating significantly.

Although the one-dimensional microvascular structure overcomes the defects of the micro/nano container, there is a lack of communication between the fiber structures, and it is difficult to achieve an efficient self-repair process. Therefore, a three-dimensional microvascular structure was proposed by scientists. Compared with the one-dimensional structure, there are multiple connection points in any position in the three-dimensional network, which improves the reliability of channel blocking.¹²⁸ It can be divided into one-component microvascular self-healing coating and multi-component interpenetrating microvascular self-healing coating according to the number of vascular networks. The one-component microvascular self-healing coating contains only a three-dimensional microvascular structure of a single healing agent, while the multi-component interpenetrating microvascular self-healing coating has a plurality of vascular structures intertwined with each other, allowing for different healing agents to be carried. In general, the latter has better self-healing performance than the former which can achieve self-repair more times. In 2007, Toohey et al.³⁵ proposed a bionic three-dimensional microvascular network structure for the first time, which opened up a new way for multiple self-healing systems, as shown in Figure 7. A self-healing epoxy coating of a microvascular network containing DCPD monomer was deposited on a high-strength metal substrate. Then, the four-point bending test was used to evaluate the healing efficiency of the material system by the recovery of the fracture toughness of the coating. Finally, the healing results of the microvascular network were compared to the data from a coating containing microencapsulated healing agents. When the catalyst concentration in the coating was 10 wt.%, cracks healed up to 7 times in the microvascular system, while microcapsule-based healing only occurred in one cycle. Therefore, compared with microcapsules, the microvascular network structure can encapsulate the coating with more healing agents and repair times. However, the healing agent of this method must be migrated and diffused over a long distance in the crack plane, which affects the efficiency of self-repair.

In 2009, Hansen et al.¹⁴⁰ embedded a three-dimensional interpenetrating microvascular network structure on an epoxy

substrate by direct writing assembly. Compared to a single network, this interpenetrating microvascular network can independently provide multiple healing agents for a given lesion, achieving at least 30 cycles of spontaneous healing. Currently, such dual microvascular networks often use epoxy resins and amine curing agents as repair agents. However, it does not react, diffuse, or cover the surface of the crack rapidly under unheated conditions. Besides, the recovery of mechanical properties also takes a considerable amount of time. In 2011, Hansen et al.¹⁴¹ doped ternary interpenetrating microvascular networks into epoxy coatings. Two of the microvascular networks were used to supply epoxy resin and curing agent, while the third microtubule network circulated the heat-regulating fluid, through which the epoxy coating was locally heated to speed up the reaction rate. It was revealed that the healing rate of the epoxy resin repair system increased obviously with the increase of temperature from 30°C to 70°C. More recently, Gergely et al.¹⁴² designed a kind of microvascular system coating for large-scale damage self-repair of the polymer coating, which can realize the complete regeneration of the coating and control the thickness of the coating accurately and autonomously. The three-dimensional interpenetrating microvascular network improved the self-healing properties of the coating. But the manufacture of these materials relied on advanced technologies such as dual direct writing and vertical printing, which was difficult to realize. Based on 3D printing technology, Postiglione et al.¹⁴³ fabricated multiple independent microvascular networks by cast water-soluble PVA mold. The structure was prepared by two-component healing chemistry whose self-healing ability was based on the proximity of the microchannels rather than interpenetrating, thus avoiding the double direct writing and vertical printing effectively.

ANTICORROSION PERFORMANCE OF THE EXTERNAL SELF-HEALING COATING

A good self-healing coating needs excellent anti-corrosion and mechanical properties. Therefore, good compatibility between the coating substrate and the packaging body is required. Otherwise, it will affect the effective release of corrosion inhibitors. Besides, the repair agent should be dispersed uniformly in the metal substrate to avoid the lack of self-healing ability in some areas of the coating. The size and number of packages will also affect the properties of the self-healing coating.^{144, 145} When the volume of the capsule is small, the number of capsules should be relatively increased to meet the needs of the repair agent. If the number of capsules is too large, the adhesion of the coating will be weakened seriously. The thickness of the microcapsule is also an important factor affecting the anti-corrosion performance of the coating. It is difficult to break under the external action if the microcapsule shell is too thick, and the inhibitor cannot be released. On the contrary, it may lead to the early release of the inhibitor and weaken the anticorrosive performance of the coating. In addition, the position of microcapsules in the coating will also affect the self-repairing performance of the coating. If the capsule is close to the metal substrate, it can effectively shorten the migration path of the inhibitor and accelerate the formation of the passivation film.¹⁴⁶

The participation of a corrosion inhibitor or healing agent ensures the anticorrosive performance of the self-repairing coating. Corrosion inhibitor mainly forms resistance film on the surface of the metal substrate through chemical action, which suppresses the cathode and anode reaction of corrosion. The healing agent mainly provides the function of a physical barrier. A non-permeable protective film is formed on the surface of the metal substrate to prevent contact with corrosive ions. As a new type of corrosion inhibitor, the BTA has excellent anti-corrosion performance for aluminum alloy. Shchukin et

al.¹⁴⁷ wrapped BTA inhibitor in polyelectrolyte nano-container by LBL, preparing a composite sol-gel coating. The intelligent anti-corrosion effect of the nano-container on aluminum alloy was verified by electrochemical means, including TEM, atomic force microscope (AFM), EIS and SVET. Zheludkevich et al.¹⁴⁸ doped SiO₂ nanocontainers encapsulated with BTA into composite sol-gel coatings. Its anti-corrosion performance to aluminum alloy is verified. Results from EIS indicated that the low-frequency impedance of the monolayer sol-gel coating without doping inhibitor decreased continuously in a 0.5 M NaCl test solution. However, the initially decreased impedance of the coating doped with corrosion inhibitor returned to the initial value after 20 minutes.¹⁴⁹ Therefore, the composite coating of doped nano-container has better long-term anti-corrosion performance than the undoped coating. Compared with the addition of only one corrosion inhibitor, the synergistic effect of multiple corrosion inhibitors can greatly improve the anticorrosive performance of the coating. Liu et al.¹⁵⁰ loaded Na₃PO₄ into the pores of Micro-arc oxidation (MAO) films. The MBT was doped into the top coating to enhance the anti-corrosion performance of the coating to magnesium alloy. First of all, through the potential test and corrosion immersion test, it is proved that Na₃PO₄ and MBT have the synergistic effect of corrosion inhibition. Then, the coatings containing different corrosion inhibitors were immersed in 3.5 wt.% NaCl for 24 hours. The coating is tested by current and analyzed by an optical microscope, as shown in Figure 8. It revealed that the coating doped with Na₃PO₄ or MBT reduced the corrosion of the substrate, compared with the MAO film without doping inhibitor. However, when Na₃PO₄ and MBT were added at the same time, the current density was significantly reduced, and no obvious corrosion occurred. Because when the self-healing coating was damaged, the MAO membrane released phosphate ions to form defective Mg₃(PO₄)₂ and Mg(OH)₂ membranes rapidly. The MBT slowly released from the top of the coating will adsorb the formed defect film and further enhance the short-term self-healing properties of the coating through synergistic action. Finally, the scratched P@MAO coating and P@MAO_MBT coating were immersed in 3.5 wt.% NaCl solution for 15 days to verify the long-term anti-corrosion performance of the double corrosion inhibitor coating.

Epoxy resin, vegetable oil, and other healing agents make full use of oxygen, water, and other substances in the environment to form a closed curing film on the surface of the metal substrate, hindering the occurrence of corrosion. Zhang et al.¹⁵¹ prepared polyurea formaldehyde microcapsules by in situ polymerization, taking fatty acid deoxy ester as a healing agent firstly. The corrosion performance of the self-healing coating was evaluated by the salt spray test and EIS. The complete epoxy coating, the scratched epoxy coating and the epoxy coating containing healing agents were immersed in 3.5 wt.% NaCl solution for different time to obtain electrochemical impedance spectroscopy, as shown in Figure 9. It can be seen from the figure that the impedance value of the complete epoxy resin coating decreases but still maintains a high order of magnitude. No obvious corrosion occurred. The scratched self-healing coating showed the same initial impedance as the intact epoxy coating. On the other hand, after the scratched epoxy coating was immersed for one hour, the impedance modulus immediately decreased to about 1×10^5 Ohm cm², indicating that the coating had failed. After 7 days, the impedance modulus of the scratched self-healing coating was still larger than that of the scratched epoxy coating. After 14 days, there were two obvious semicircles in the Nyquist plot of the scratched self-healing coating, indicating that the corrosive ions were in contact with the matrix and the corrosion began to occur. However, it provided longer corrosion resistance than scratched epoxy coatings. It was consistent with the results of the salt spray test. The leakage of unreacted healing agents often leads to environmental problems. Vegetable oil as an eco-friendly healing agent, which has been widely used. Taking coconut oil-

based alkyd resin (CAR) as a healing agent, Ataei et al.¹⁵² produced alkyd resin-based microcapsules by in-situ polymerization which were applied to epoxy resin coating. The anticorrosive properties of different concentrations of microcapsules on the steel plate were explored. The results of potential dynamic polarization and electrochemical impedance spectroscopy showed that when the concentration of microcapsule was 10 wt.%, the amount of CAR released was enough to repair the crack and protect the steel matrix from corrosion. At this time, the anti-corrosion performance of the metal substrate was the best. In this study, the anti-corrosion performance of the coating can be improved by adding a small amount of microcapsules.

Applying the corrosion inhibitor and healing agent to the same coating also can improve the corrosion inhibition of the coating. Habib et al.¹⁵³ embedded NaNO₃ corrosion inhibitor and LO healing agent into nano-polymer coating at the same coating. Its anti-corrosive effect on metal was studied. HNTs carried NaNO₃ corrosion inhibitor and the LO healing agent was stored in urea-formaldehyde microencapsulated (UFMC). Pure coating, plain coating, and smart coating were immersed in 3.5 wt.% NaCl solution for corrosion test, which all contained microcapsules and HNTs. The EIS results showed that, among them, the intelligent anticorrosive coating containing both NaNO₃ corrosion inhibitor and LO healing agent had the highest resistance value, and its anticorrosive performance was the best. In addition, the anti-corrosion performance of the composite coating was related to the type of repair agent and coating. And the corrosion inhibitor and healing agent could produce a synergistic effect only when the ratio was appropriate. Mahmoudian et al.¹⁵⁴ selected two kinds of corrosion inhibitor (BTA and potassium ethyl xanthate) and coating material (epoxy and polyurethane). The composite self-healing anticorrosive coating was prepared by mixing different contents of LO-based nano-capsules and corrosion inhibitors into the coating substrate. The self-healing and anticorrosive properties of copper were compared. The results of EIS and microscope indicated that the performance of the composite coating was the best when 3 wt.% nano-capsules and 5 wt.% ethyl potassium xanthates were used as repair agent and polyurethane as the coating substrate. The increase of the content of the repair agent would weaken the adhesion of the coating, thus reducing the anti-corrosion performance of the coating.

What is more, the preparation of multi-functional anti-corrosion coating is of great significance to improve the anticorrosive performance of coatings. Lutz et al.¹⁵⁵ blended MBT-loaded LDH into an acrylated polycaprolactone polyurethane-based shape-recovery coating for the protection of hot-dip galvanized steel (HDG). The corrosion protection mechanism under the dual effects of corrosion inhibitor release and shape memory is described in detail, as shown in Figure 10. On the one hand, in the corrosion environment of NaCl solution, Cl⁻ exchanges with MBT anions, MBT is released, covering the exposed metal surface, and inhibiting the corrosion process. On the other hand, heating the coating for 2 minutes to 60°C can produce sufficient fluidity, automatically close defects caused by the machine, and restore the structure and performance of the coating. If Cl⁻ has reached the metal surface before the coating is deformed, MBT will be released, forming a protective layer on the metal surface. It needs to be stated that these two mechanisms are independent of each other, and the shape recovery mechanism can still play a role after the corrosion inhibitor is released.

Qian et al.¹⁵⁶ developed a new type of self-repairing superhydrophobic coating under the dual action of epoxy shape memory polymer (SMP) and corrosion inhibitor BTA. After scratching the superhydrophobic coatings containing different concentrations of BTA, the superhydrophobic coatings were immersed in 3.5 wt.% NaCl

solution for EIS measurement. The results showed that the number of corrosion products decreased obviously with the increase of BTA content. This may be due to the increase of the coverage area of the BTA adsorption layer, resulting in the improvement of sustained-release efficiency. Besides, the heat-induced shape memory effect of epoxy coating can also improve the corrosion resistance of the epoxy coating. The micro-corrosion morphology revealed that, compared with the common scratch coating, the corrosion product of the hot repair coating was less. And the corrosion performance was improved obviously. In order to further demonstrate the shape memory effect and the healing effect of corrosion inhibitor, the scanning electrochemical microscope (SECM) was used to monitor the corrosion reaction in situ, as shown in Figure 11. For ordinary scratch coatings, there were varying degrees of corrosion. However, after soaking for three days, the corrosion degree of scratched BTA-5% coating was lower than that of scratched BTA-free coating significantly. This is due to the corrosion inhibition of BTA. For the coating after a hot repair, the damaged area in the coating was reduced significantly because of its crack closure ability. The degree of corrosion was much lower than that of other similar situations. However, corrosive media can penetrate closed cracks and corrode the metal substrate eventually. Therefore, the coating containing SMP can only temporarily weaken the corrosion of metal, but cannot completely inhibit the corrosion.

EXISTING INADEQUACIES

A large amount of healing agents is needed to form a resistant reticulated film in the defect site. Therefore, improving the repair capacity of micro/nano containers is the primary issue. For organic microcapsules, one can increase the load of the repairing agent by increasing the number or size of the capsules. However, this also brings some problems. First of all, adding a large number of microcapsules to the coating may cause the microcapsules to gather in a certain area and make some areas of the coating lose the ability of self-healing. Mechanically, each microcapsule acts as a spherical space, effectively creating a stress concentration. Therefore, each microcapsule is a potential crack-inducing point. Secondly, in terms of microcapsule size, too large can make it so the coating can achieve the correct thickness profile according to manufacturer directions, too small can aggregate and make an uneven coating. So there is an ideal size of such microcapsules that cannot be so large, above 60 μm , neither so small, below 1-20 μm . Although the use of larger size microcapsules can increase the carrying capacity, it reduces the compatibility of the capsules with the coating. Surface modification of micro/nano containers is an effective method to improve the interface performance between the micro/nano container and the coating substrate. Tong et al.¹⁵⁷ studied the effect of silane coupling agent (KH550) on polymelamine-urea-formaldehyde resin (MUF) microcapsules. The results of the SEM test showed that compared with the microcapsules before modification, the interfacial properties of the microcapsules modified by KH550 were significantly improved. It has better compatibility and dispersion. The compatibility of microcapsules with a coating substrate was also related to the types of modifiers. Es-haghi et al.¹⁵⁸ adopted (3-aminopropyl)-trimethoxysilane (APS), [3-(methacryloyloxy)-propyl]-trimethoxysilane (MPS) and [3-(2,3-epoxypropoxy)-propyl] trimethoxysilane (EPS) to improve the compatibility of ethyl cellulose microcapsules with polymer matrix. The results indicated that the microcapsules modified by APS had better compatibility with the coating as well as mechanical properties and self-repairing properties.

Unlike organic microcapsules, the volume of inorganic micro/nano containers is often fixed. We can improve the bearing capacity of inorganic micro/nano containers by expanding the internal space of inorganic micro/nano containers.¹⁵⁹ Gaaz et al.¹⁶⁰ studied the effect of

sulfuric acid on the physical and chemical properties of HNT by exposing it to sulfuric acid solution for different times. Results from the field emission scanning electron microscopy (FESEM) indicated that sulfuric acid dissolves the AlO_6 octahedral layer, resulting in breakdown and collapse of the SiO_4 tetrahedral layer, producing porous nanorods. With the increase of acid time, HNT nanotubes began to be separated, and the surface area and pore volume increased. The mixing of HNT nanotubes was obvious until 21 hours later. What is more, the modification of micro/nano containers can also increase the loading capacity. Tan et al.¹⁶¹ used interlayer methoxy modification to increase the loading capacity of amitrole (AMT). The loading and release properties of halloysite (Hal) and kaolinite (Kaol) for AMT were compared, as shown in Figure 12. The modification increased the attraction between AMT and Hal/Kaol as well as attracting part of AMT to be embedded between Hal/Kaol interlayers so that the load capacity of Hal/Kaol was improved. At the same time, the unique cavity of Hal made it have more load than Kaol. In addition, unlike Hal, methoxy modification had an obvious inhibitory effect on the release of AMT from Kaol. This is due to the long diffusion path of the layered structure and the electrostatic interaction between the layers will hinder the release of AMT. As a result, the load and release capacity of micro/nano containers are also related to the shape of the container itself.

The microvascular system has a larger space volume than the micro/nano container, which is closer to the concept of bionic self-repair in theory. However, there are still many problems to be solved. Unlike micro/nano containers, for vascular network materials, repair agents are introduced after the network is integrated into the matrix. Therefore, the restoration agent is required to have good fluidity and wettability which is compatible with blood vessels and has strict requirements for shell materials. Besides, control the size of the vascular structure reasonably. The diameter of blood vessels should not be too small, otherwise many repair agents are easy to cause blockage of blood vessels. If the diameter of the blood vessel is too large, it will lead to the larger microvascular network structure, which is not suitable for thinner anticorrosive coating.

Besides, the effective release of the healing agent can enhance the active anticorrosive ability of the self-repairing anticorrosive coating. Taking inorganic nano-containers as an example, since the inorganic nano-container generally has an open pore structure, it is difficult for the repair agent to achieve efficient storage and release. Therefore, scientists consider installing nano-valves on the surface of nano-containers to achieve control of the repair agent. When the local pH of the coating changes, the nano-valve opens and releases the repair agent in the container, thus avoiding the waste caused by the premature release of the repair agent.^{162, 163} For the first time, Chen et al.¹⁶⁴ attached two acid-base responsive supramolecular nano-valves to the surface of hollow silica nanocontainers (HMSNs) in a covalent bond and self-assembled to form pH-responsive nanocontainers, which were dispersed in a zirconium-silicon sol-gel composite coating uniformly. The nano-valve opened in response to the increase or decrease of local pH caused by metal corrosion reaction. Then the corrosion inhibitor in the container was released quickly. And a dense film formed on the surface of the damaged alloy, which hinders the occurrence of corrosion. Compared with the ordinary silica nano-container, the modified nano-container had a larger cavity structure, which improved the load capacity and compatibility of the container. Results from the EIS indicated that the sol-gel coating doped with pH-responsive nano-container had long-term anti-corrosion performance compared with the undoped. Fu et al.¹¹⁰ installed supramolecular nanovalves in the form of bistable pseudorotaxanes on the outer surface of hollow mesoporous silica nanoparticles (HMSs), achieving pH response control of caffeine molecules, as shown in Figure 13. In a

near-neutral pH environment, through the ion-dipole interaction, cucurbit [7] macrocycles thread onto the hexylammonium recognition site by ion-dipole interaction, plugging the pores, and achieving zero release of caffeine molecules. With the decrease of pH, the cucurbit [7] macrocycle gradually shuttled to the recognition site of ferrocenecarboxylic acid. The directional movement of the cucurbit [7] macrocyclic ring opens the supramolecular nanovalve, providing a way for the diffusion of corrosion inhibitors. With the increase of pH, the cucurbit [7] macrocyclic structure gradually detached from the stem, causing the corrosion inhibitor to be released from the pores. The experimental results of SVET show that the smart nanocontainer with acid-base dual excitation response characteristics can simultaneously inhibit the corrosion activities in the micro-anode and micro-cathode regions, and shows good self-healing function.

In practical engineering applications, the anti-corrosion performance of the system is often enhanced through the synergy of cathodic protection and coating systems. Baird et al.¹⁶⁵ first synthesized $23 \pm 10 \mu\text{m}$ polyurea microcapsules filled with octadecyltrimethoxysilane (OTS), a liquid self-healing agent, and added them to a primer rich in zinc, a cathodic protection agent. The synergy between self-repair and cathodic protection was studied by electrochemical means. When the coating is damaged, corrosive substances begin to invade the coating and come into contact with the metal substrate. At this time, due to the existence of cathodic protection, corrosion is first suppressed and the metal surface is retained for a sufficient time. Therefore, OTS can be directly bonded to the metal substrate instead of corrosion products. Finally, a strong barrier layer is formed on the exposed metal surface to protect the base metal from corrosion. In addition, the combination of OTS and zinc reduces the oxidation rate of zinc, prolongs the lifetime of galvanic protection. However, for pH-controlled self-healing coatings, cathodic protection will cause a significant change in pH, which may lead to the premature release of pH-based self-healing coatings. So far, reports on this issue have not been found.

Most importantly, the high cost of self-healing raw materials and the environmental problems derived from them are the main factors restricting their industrial application. The recycling and reuse of waste solve the above problems well.¹⁶⁶ Liu et al.¹⁶⁷ prepared a self-healing hydrogel composed of porous carbon-based microcapsules from fruit residue, as shown in Figure 14. The preparation of the coating was divided into two steps. First, glutaraldehyde (GA) was encapsulated in porous carbon (PC) made from fruit residue, and polydopamine (PDA) was coated on the outer layer to obtain microcapsules. Then the functional self-healing hydrogel coating was prepared by in-situ polymerization by adding microcapsule and Fe^{3+} into acrylic acid (AA) and acrylate-guar gum (AGG) respectively. The coating has both extrinsic and intrinsic healing dual healing mechanism. When the coating was damaged, GA would release from the microcapsule as a cross-linking agent and react with modified guar gum to repair the microcracks in the hydrogel. At the same time, PDA on the surface of microcapsules can repair hydrogels through synergistic action continuously. This kind of self-repairing hydrogel coating not only realizes the reuse of fruit residue but also improves the self-healing performance of the coating, which has a good development prospect in the field of metal anti-corrosion.

SUMMARY AND OUTLOOK

This review provides a comprehensive discussion on the preparation, self-healing properties and anti-corrosion mechanisms of the external self-healing coating. The features of external self-healing coatings are shown in Table 1.

For the micro/nano container-based self-healing coating, the main problems are limited load capacity and uneven dispersion of the micro/nano container. It is popular to increase the load capacity by increasing the volume, but it weakens the compatibility between the container and the coating. Increasing the number of micro/nano containers is also an effective method, while it means introducing more defects, which will damage the corrosion performance of the coating. What is worse, a large number of micro/nano containers are easy to aggregate. The vascular network self-healing coating overcomes the shortcoming, which can repair large size cracks more than once. Nevertheless, the vascular network-based self-healing coating has strict requirements on the properties of shell materials, which hinders its application in industrial production. The external self-healing coating is still a hot topic in the future, and its development trend can be summarized as follows:

- ❖ Optimize the original self-healing system. Firstly, looking for economic, environmentally friendly and sustainable healing agents to improve the industrial application of self-healing coatings is pressing. Secondly, optimizing the loading capacity and dispersion of containers by coating modification or surface modification is also necessary. Finally, it is trendy to improve the performance of the coating by reducing the container from micron to nanometer.
- ❖ Combine the original self-healing system. The coating system with external and intrinsic healing mechanisms, or the micro/nano container and microvascular network will be applied to the coating substrate at the same time, to improve the anticorrosion performance of the coating.
- ❖ Design multi-responsive or multi-functional coatings. The transition from single responsive coatings to multi-responsive coatings is promising. Because the single responsive coating does not have a high self-healing efficiency, and the repair agent cannot be released timely. The appearance of multi-responsive coating solves the above problems precisely. In addition, the emergence of self-healing, anticorrosive, super-hydrophobic and other multi-functional coatings can also solve the problems we are facing.
- ❖ Perfect coating evaluation system. At present, most research reports only focus on the short-term application effect of self-healing coatings. Such papers do not show challenging tests as sulfide stress cracking for long exposition time or cyclic tests, or even field tests. Therefore, more stringent long-term or accelerated corrosion tests are needed to evaluate the performance of coatings.

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FIGURE CAPTIONS

- FIGURE 1. The corrosion inhibitor microcapsule-based self-healing coating.⁷⁴
- FIGURE 2. Schematic illustration of the fabrication of DCPD@PF capsules.⁸³
- FIGURE 3. Schematic diagram of sunlight-induced self-healing of polymeric microcapsules with ESO-based core materials embedded into epoxy coatings.⁹⁷
- FIGURE 4. Traditional multi-step method and the one-step route presented in this work.¹¹⁸
- FIGURE 5. Profile of the benzoate anion (a) and chloride anion concentration (b) in 3.5 wt.% NaCl solution; XRD pattern (c) and FT-IR spectrum (d) of sample reclaimed from 3.5 wt.% NaCl solution containing BZ-LDHs.¹²⁴
- FIGURE 6. Preparation of hollow fiber by electrospinning: (a) coaxial electrospinning; (b) emulsion electrospinning.^{135, 136}
- FIGURE 7. Schematic diagram of the coating structure of a three-dimensional microvascular network.³⁵
- FIGURE 8. The current density distributions (a, b, c, d) and optical morphologies (e, f, g, h) of the damaged inhibitor-containing coatings immersed in 3.5 wt.% NaCl for 24 h.¹⁵⁰
- FIGURE 9. Bode and Nyquist plots of the intact epoxy coating, the scratched epoxy coating (1.0 cm scratch length), and the self-healing coating with 1.0 cm scratch length. Bode plots of samples after different immersion time: (a) 1 h, (b) 1 day, (c) 7 days, and (d) 14 days. Nyquist plots of (e) the self-healing coating and (f) the intact epoxy coating.¹⁵¹
- FIGURE 10. Working mechanism of a multi-action self-healing (MASH) coating (A): when a MASH coating is scratched (B) two independent actions can follow: (1) the scratch is closed by heating the sample and restoring the coating barrier (C). (2) If a solution containing, for example, aggressive chloride ions reaches the defect, the corrosion inhibitor MBT is released from LDH in exchange for the chloride ions. The released MBT forms a protective layer protecting the metal substrate (D). Eventually, the scratch closing action by heating can still be triggered to prevent continuous access of aggressive ions (E).¹⁵⁵
- FIGURE 11. (a) SECM maps of (a1) the original BTA-free coating surfaces and the scratched BTA-free coating surfaces immersed in a 3.5 wt.% NaCl solution for (a2) 1 day and (a3) 3 days. (b) SECM maps of (b1) the original BTA-5% coating surfaces and the scratched BTA-5% coating surfaces immersed in a 3.5 wt.% NaCl solution for (b2) 1 day and (b3) 3 days. (c) SECM maps of the healed BTA-5% coating surfaces immersed in a 3.5 wt.% NaCl solution for (c1) 0 days, (c2) 1 day and (c3) 3 days.¹⁵⁶
- FIGURE 12. Schematic representation of AMT loading and release in methoxy-modified.¹⁶¹
- FIGURE 13. (A) Schematic illustration of the working mechanism for the mechanized HMSs; release profiles of caffeine molecules from the mechanized HMSs under acidic conditions (B) and alkaline conditions (C).¹¹⁰
- FIGURE 14. Functional self-repairing hydrogel coating: (a) preparation of micro-capsules; (b) coating preparation; (c) repair mechanism.¹⁶⁷

Figures

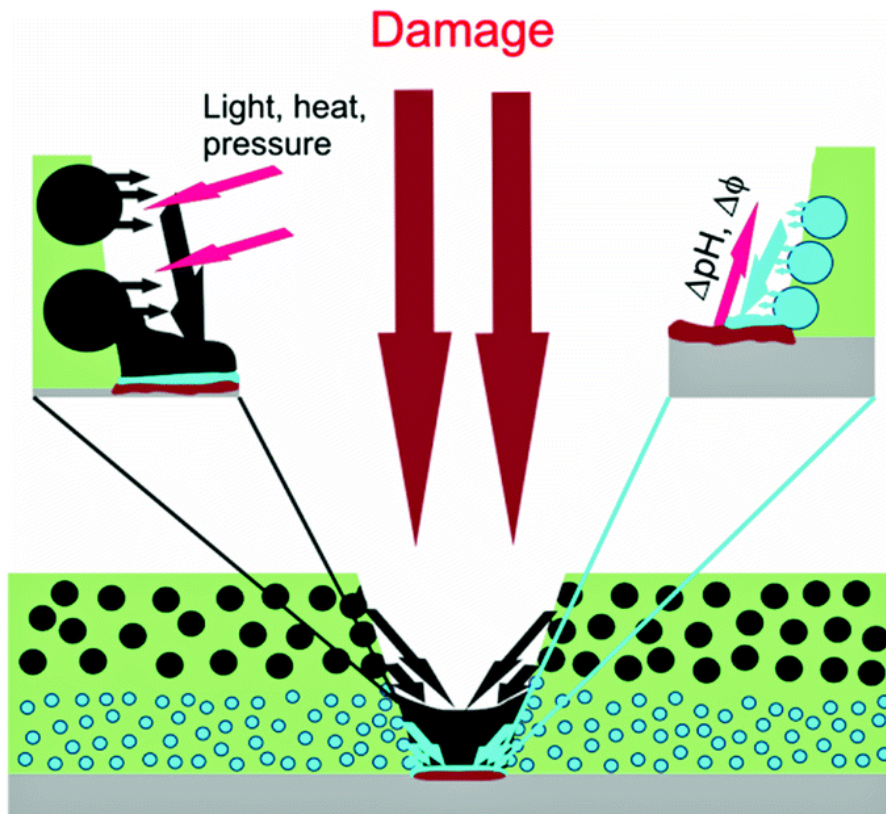


Figure 1. The corrosion inhibitor microcapsule-based self-healing coating.

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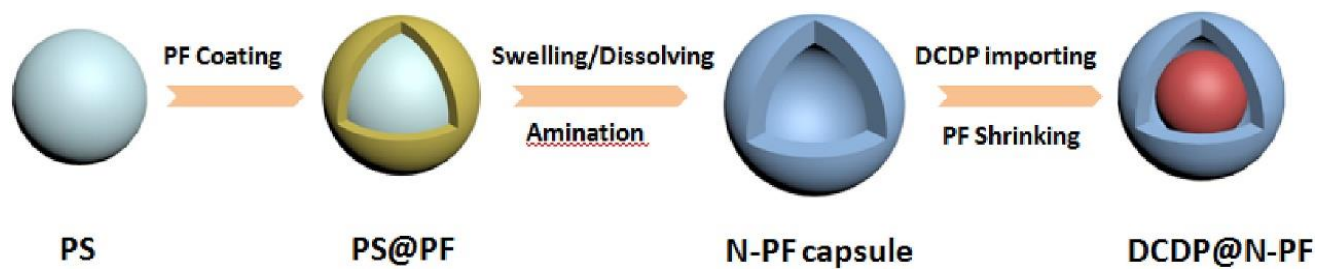


Figure 2. Schematic illustration of the fabrication of DCPD@PF capsules.

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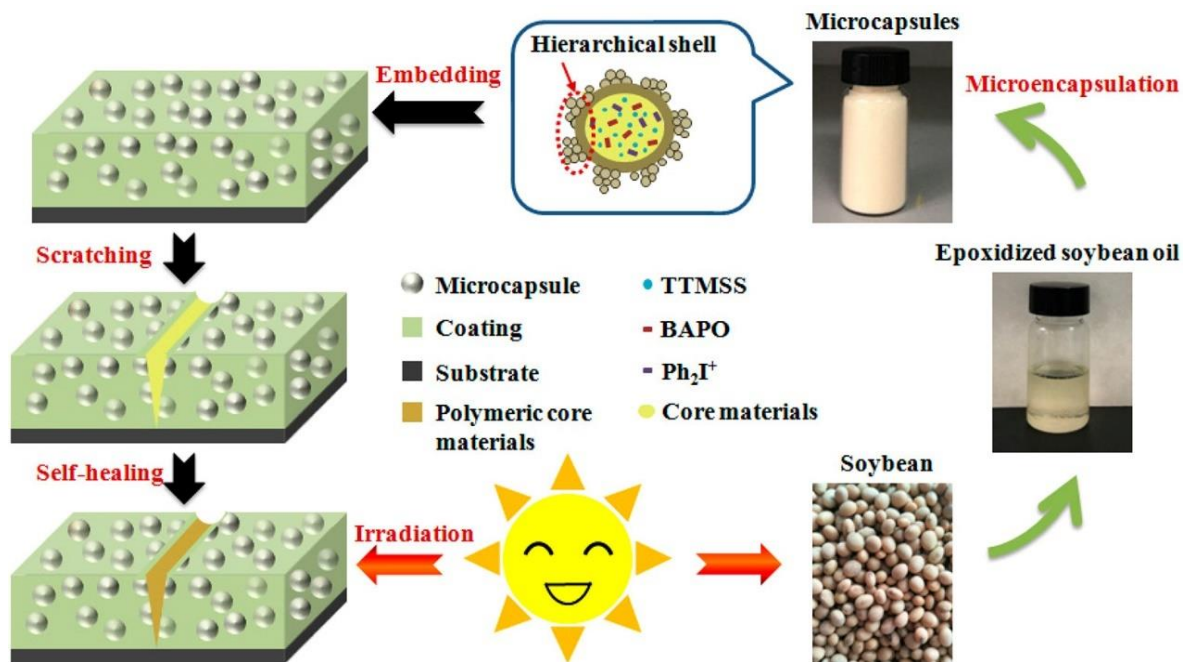


Figure 3. Schematic diagram of sunlight-induced self-healing of polymeric microcapsules with ESO-based core materials embedded into epoxy coatings.

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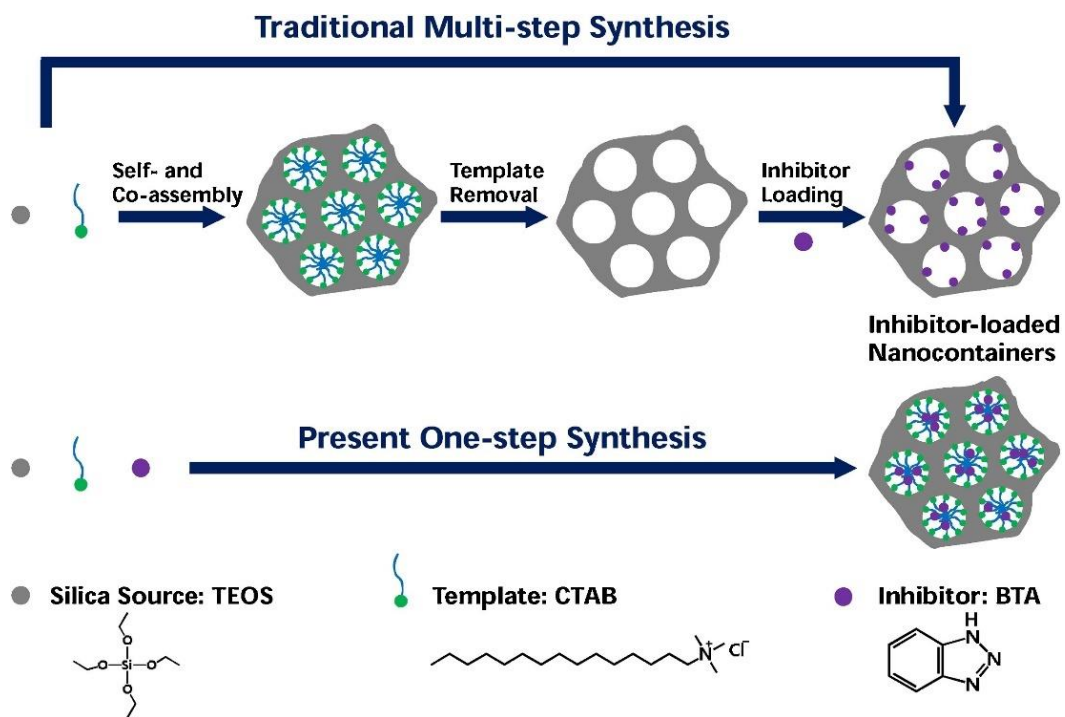


Figure 4. Traditional multi-step method and the one-step route presented in this work.

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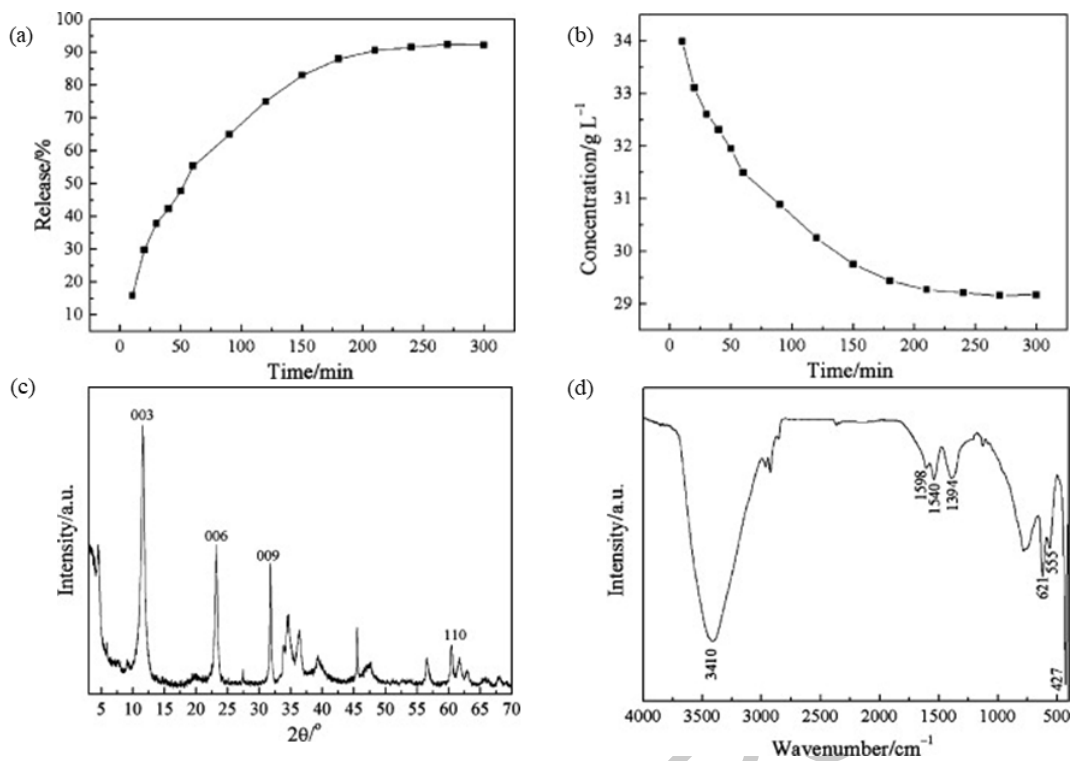


Figure 5. Profile of the benzoate anion (a) and chloride anion concentration (b) in 3.5 wt.% NaCl solution; XRD pattern (c) and FT-IR spectrum (d) of sample reclaimed from 3.5 wt.% NaCl solution containing BZ-LDHs.

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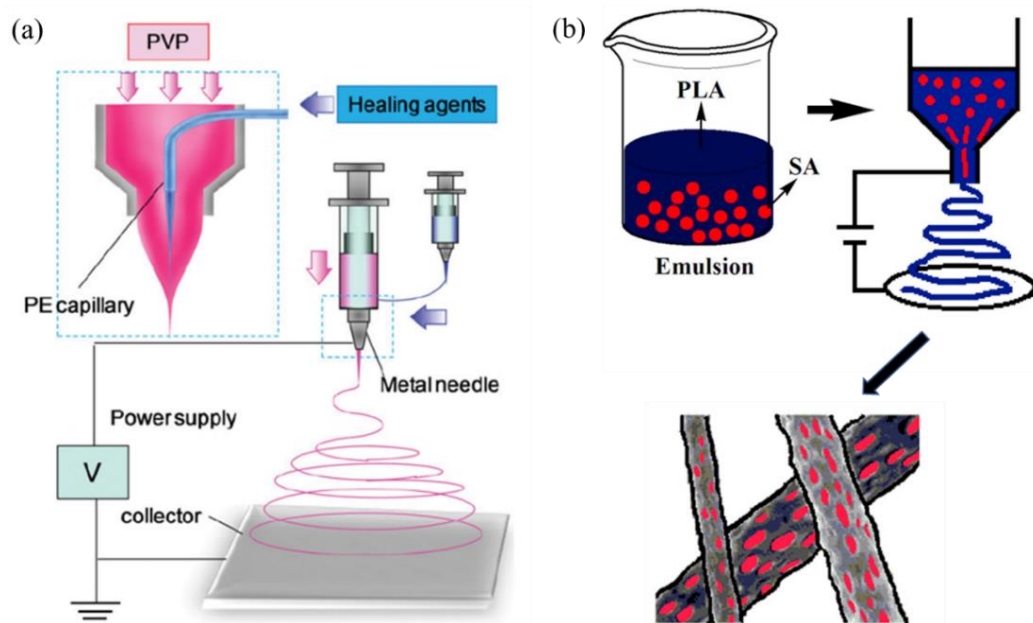


Figure 6. Preparation of hollow fiber by electrospinning: (a) coaxial electrospinning; (b) emulsion electrospinning.

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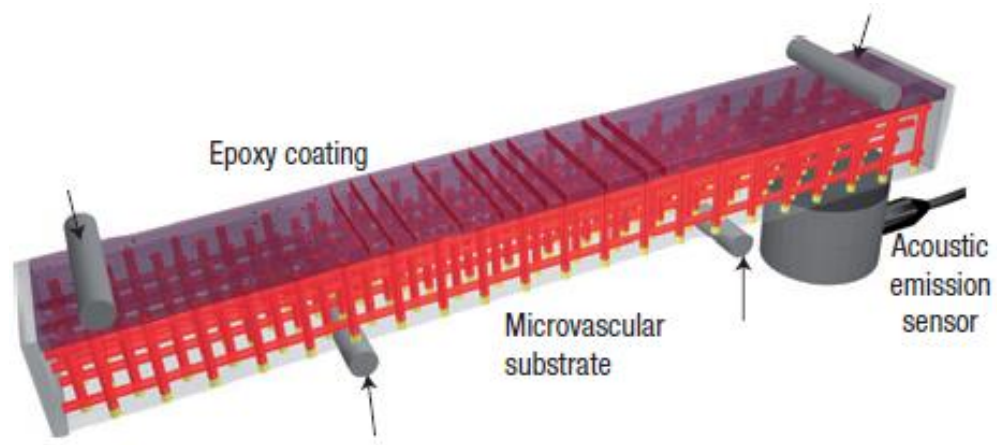


Figure 7. Schematic diagram of the coating structure of a three-dimensional microvascular network.

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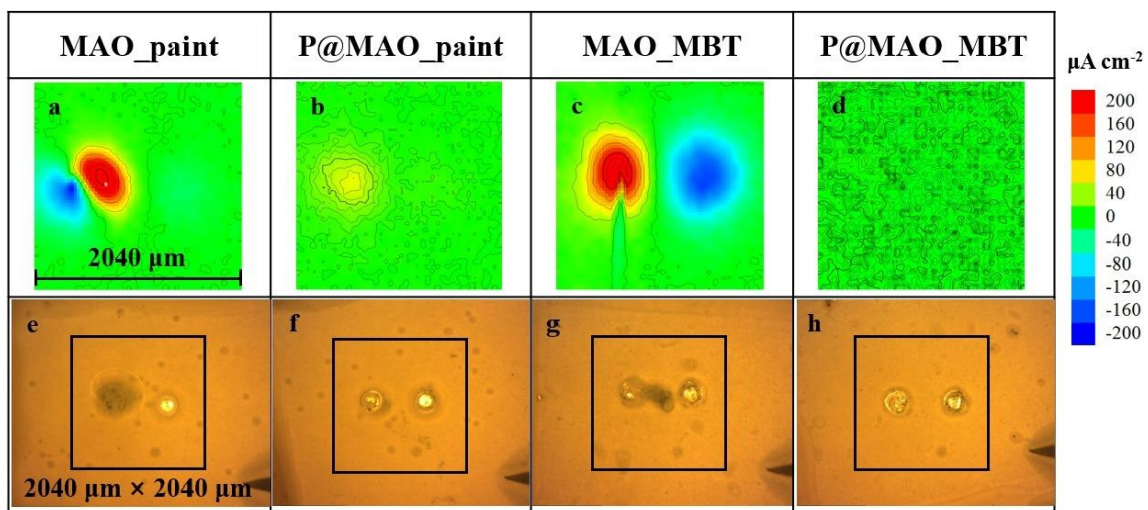


Figure 8. The current density distributions (a, b, c, d) and optical morphologies (e, f, g, h) of the damaged inhibitor-containing coatings immersed in 3.5 wt.% NaCl for 24 h.

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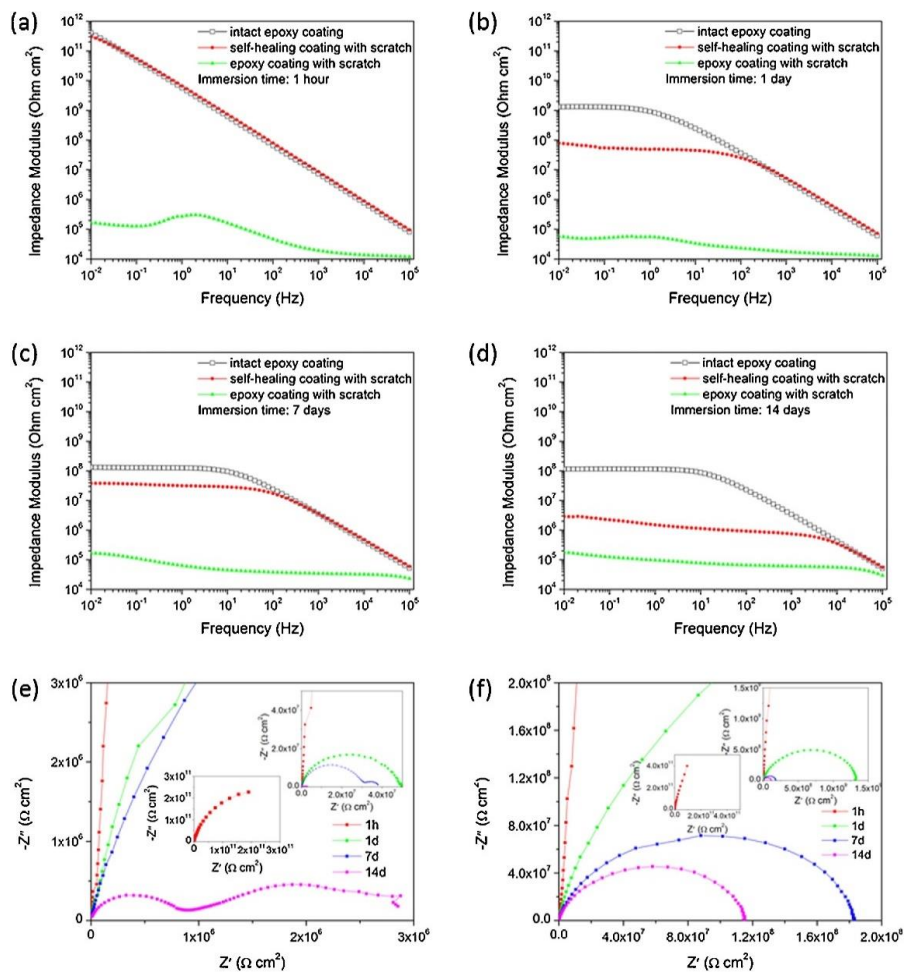


Figure 9. Bode and Nyquist plots of the intact epoxy coating, the scratched epoxy coating (1.0 cm scratch length), and the self-healing coating with 1.0 cm scratch length. Bode plots of samples after different immersion time: (a) 1 h, (b) 1 day, (c) 7 days, and (d) 14 days. Nyquist plots of (e) the self-healing coating and (f) the intact epoxy coating

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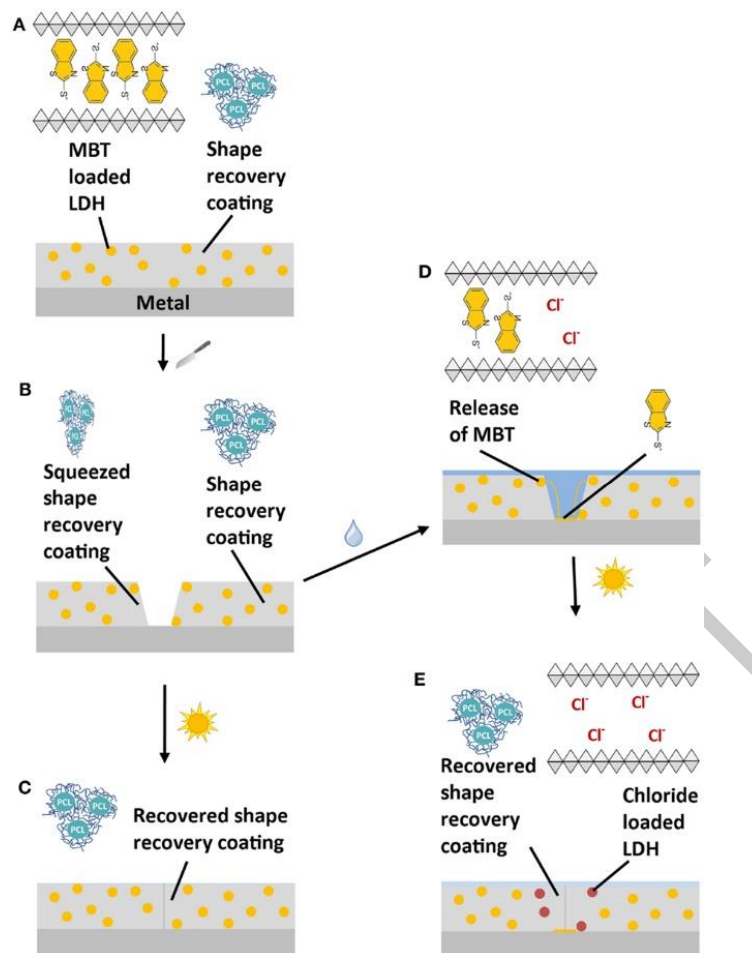


Figure 10. Working mechanism of a multi-action self-healing (MASH) coating (A): when a MASH coating is scratched (B) two independent actions can follow: (1) the scratch is closed by heating the sample and restoring the coating barrier (C). (2) If a solution containing, for example, aggressive chloride ions reaches the defect, the corrosion inhibitor MBT is released from LDH in exchange for the chloride ions. The released MBT forms a protective layer protecting the metal substrate (D). Eventually, the scratch closing action by heating can still be triggered to prevent continuous access of aggressive ions (E).

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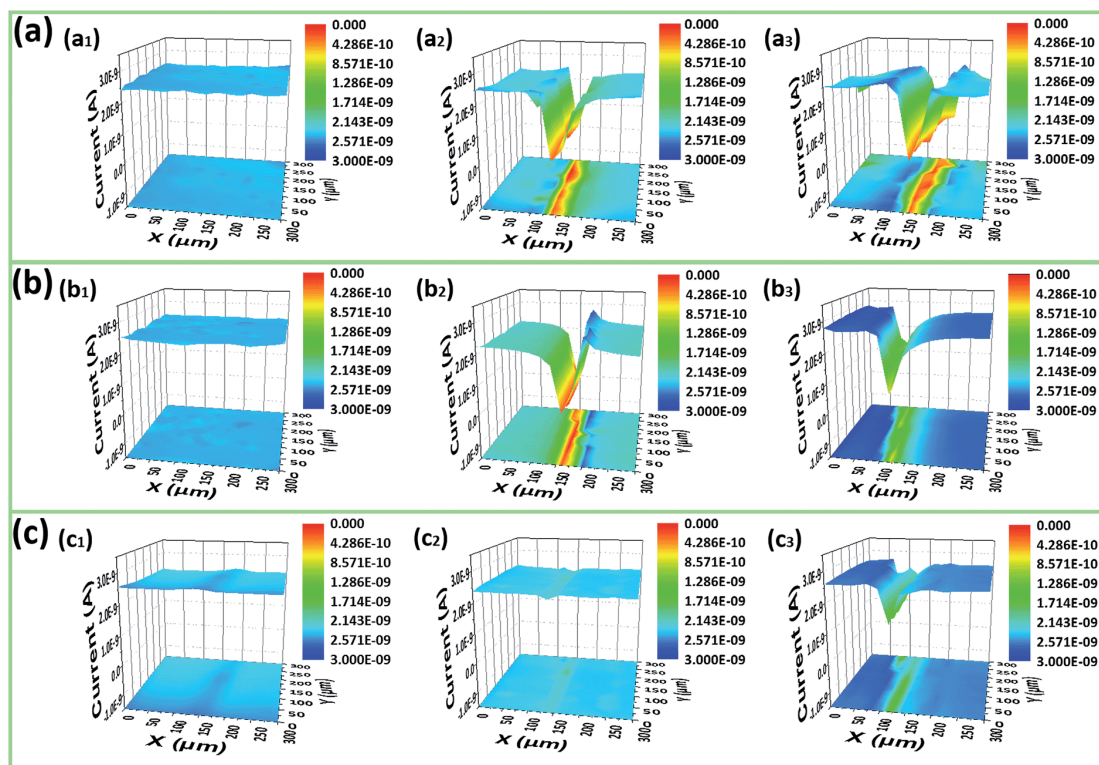


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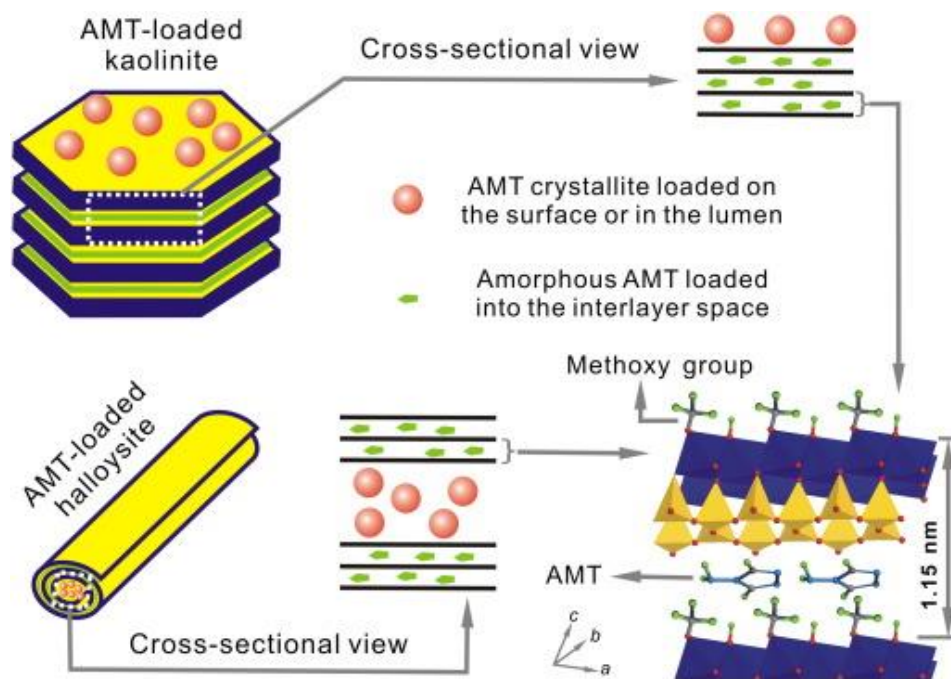


Figure 12. Schematic representation of AMT loading and release in methoxy-modified.

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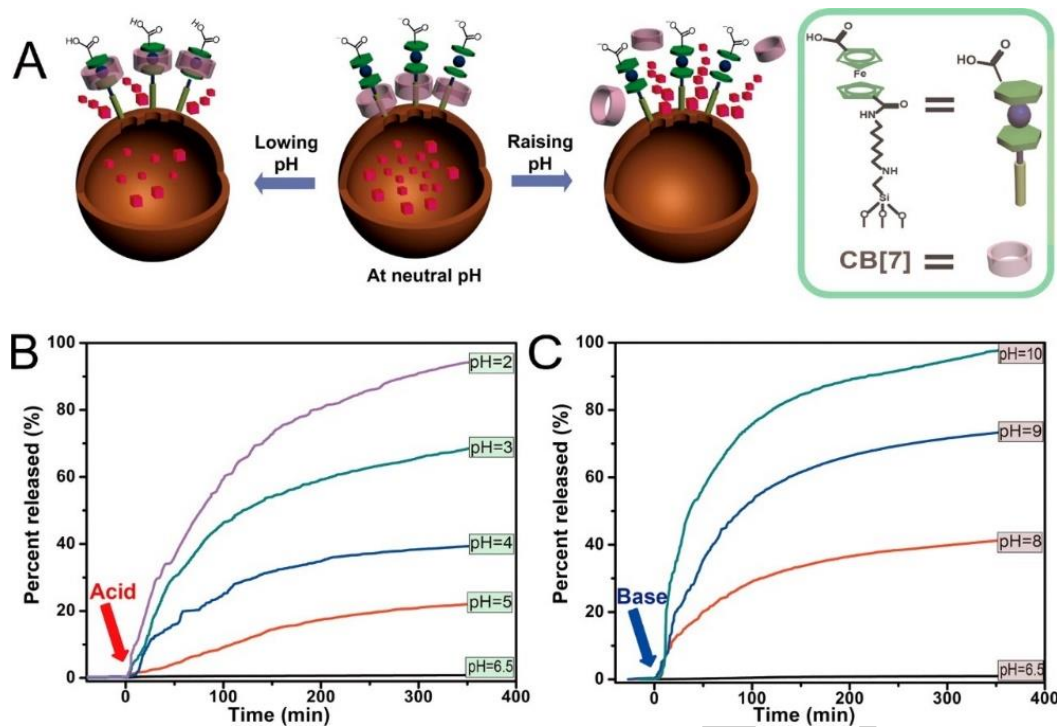


Figure 13. (A) Schematic illustration of the working mechanism for the mechanized HMSs; release profiles of caffeine molecules from the mechanized HMSs under acidic conditions (B) and alkaline conditions (C)

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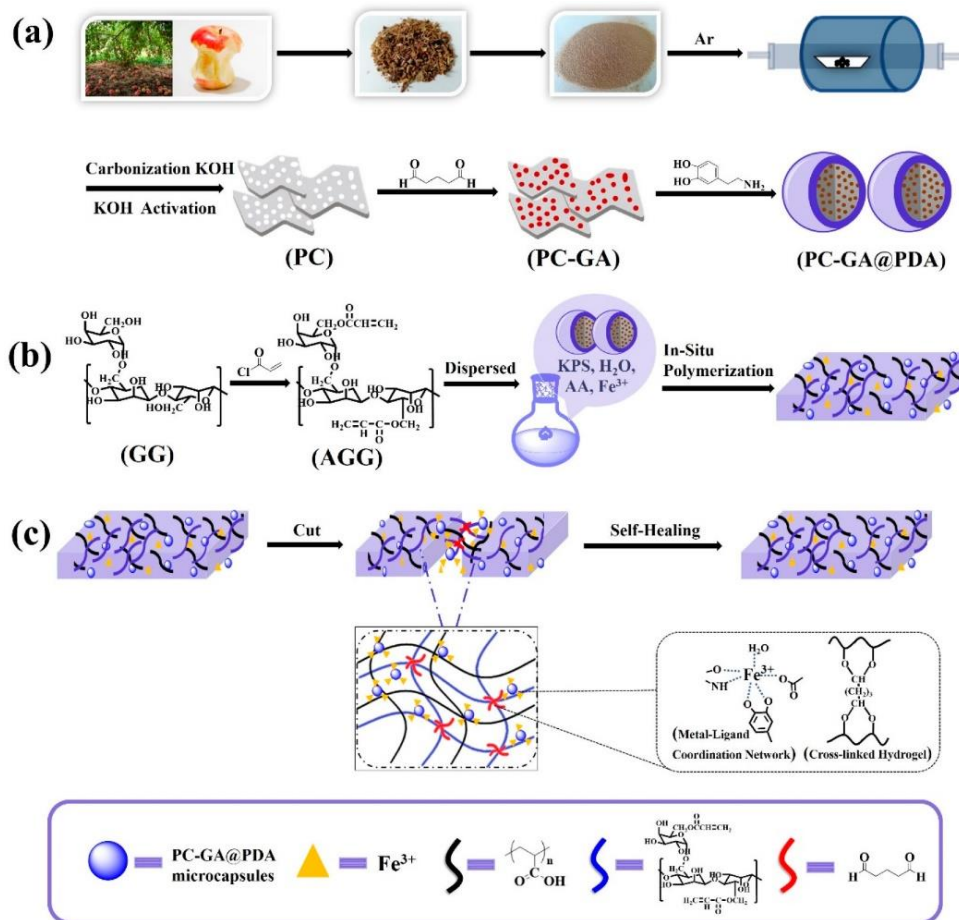


Figure 14. Functional self-repairing hydrogel coating: (a) preparation of micro-capsules; (b) coating preparation; (c) repair mechanism.

Tables

Table 1. Features between all different coating types.

Types	Preparation	Advantages	Disadvantages
Organic micro/nano containers	In situ polymerization; Interfacial polymerization; Emulsion polymerization; Sol-gel, etc.	Simple preparation process; Various available materials	Poor uniformity/density; Negative effect on mechanical properties
Inorganic micro/nano containers	Ion exchange method; Co-precipitation method, etc.	Simple preparation process; Strong processability	Poor uniformity/density; Weak controlled release
Microvascular network	Electrospinning; Solution blowing; Direct writing; 3D printing, etc.	High density; Positive effect on mechanical properties	Limited raw materials

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