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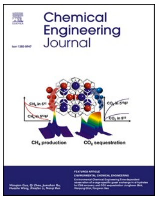

Review

Micro/nanocontainer-based intelligent coatings: Synthesis, performance and applications – A review

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ABSTRACT

Metal corrosion causes huge economic losses, environmental pollution and industrial disasters. Application of smart self-healing coatings for the active corrosion protection of metal substrate has attracted substantial interest in recent years. The self-healing function can be achieved through either the intrinsic or extrinsic method. The intrinsic self-healing coatings mainly make use of the reversible physical and chemical interactions between molecules, whose self-healing effect is permanent. While the extrinsic method is mainly caused by embedding the micro/nanocontainers in the coatings, which can sense the micro-environmental changes and give rapid feedback to repair the micro cracked zones on the coating surface, the self-healing performance is temporary after the encapsulated active substances are fully consumed. Furthermore, inspired by these intelligent behaviors, more and more multi-functional coatings are designed and widely used in different fields. In this review, we summarized the research development of different stimuli-responsive self-healing coatings based on micro/nanocontainer techniques in recent years. Different types of micro/nanocontainers, as well as their synthesis or encapsulation technologies, are exampled to clarify the recent achievements. Meanwhile, the single stimulus-responsive systems are gradually evolved into the multi-stimulus-responsive system that endows the coatings with more sensitivity and intelligence. The stimuli-responsive self-healing coatings with different functions, such as self-reporting, anti-microbial, anti-fouling and self-lubrication functions, etc., are also explored, which enriches the application ranges of these smart coatings. This review investigated the research progress of the micro/nanocontainers-based self-healing coatings over the past few years and provided a unique insight into the future development of such smart coatings.

1. Corrosion protection: from physical barrier to active protection

Metal corrosion leads to a huge economical loss every year and also has a great negative impact on our daily life. The application of anticorrosive coatings is the most convenient and effective strategy to protect the metal against degradation. Traditional corrosion protective coatings mainly create a physical barrier to prevent the direct contact of the corrosive ions and water with the metal substrate. This kind of physical barrier effect is also regarded as passive corrosion protection. However, the coating structure may be attacked by the corrosive ions and stimulated by the external environment changes as the prolonged service time in the aggressive environment. All these factors will lead to the appearance of the micro-pores and cracks across the coating surface, the aggressive ions will penetrate and diffuse through these defects and arrive at the metal surface, finally causing the degradation of the coating matrix and corrosion of the underlying metals. As the service time extends, the micro-corrosion sites will be enlarged, leading to failure of the protective coatings and severe corrosion of the metal substrate. Therefore, the coatings with only a physical barrier effect cannot play long-term corrosion protective ability in many cases especially when a harsh environment is combined with mechanical impacts.

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Numerous methods have been carried out to extend the service time of the coating and improve the corrosion protection efficiency. Recently, the concept of ‘smart self-healing coatings’ has been proposed and widely investigated, which can be achieved through intrinsic or extrinsic self-healing methods. The intrinsic self-healing coatings are based on the break and reorganization of the chains, and therefore achieving the autonomous self-healing effects at the molecular level, which is an inherent characteristic of the material itself. While the extrinsic self-healing method is achieved by incorporating the active species (such as corrosion inhibitors and healing agents) to inhibit corrosion activity or repair the coating structures. These coatings can provide a physical barrier to resist the ingress of the water, oxygen and aggressive corrosive ions, moreover, the incorporated active species will also minimize the occurrence of corrosion reactions at the metal/electrolyte interface when the physical barrier effect is disrupted [1]. Overall, incorporating the active healing species in the coating transforms the ‘passive corrosion protection’ system into ‘active corrosion protection’ that the corrosion inhibition actions are activated when the coating upon damaged [2].

However, the main drawback of this kind of active corrosion protective coating is that the self-healing function is temporary when the active species are fully consumed. And the poor compatibility with the polymeric matrix and the possible reactions between the active species and polymeric matrix will cause the disordered and uncontrolled release of the incorporated active species, which will further impair the coating performance. In addition, from an economic and environmental standpoint, chromate-based coatings are also banned in recent years by many countries since the high toxicity and carcinogenic effects of chromium (VI) may cause major damage to the environment and seriously endanger human health.

The intelligent active corrosion protection coatings based on micro/nanocontainers are designed in recent years. The active substances are pre-loaded in the containers and then dispersed in the polymeric matrix. The micro/nanocontainers can respond to one or several stimuli from the environmental changes and give rapid feedback. As a result, the encapsulated active species are triggered to release to repair the coatings and therefore inhibit further corrosion. This kind of ‘active corrosion protection’ system for the metal substrate has also gradually become a popular research trend, and numerous kinds of micro/nanocontainers are designed to achieve their multi-functions. In this review, we summarized the research progress of the micro/nanocontainers-based intelligent coatings in recent years (Fig. 1). Different types of micro/nanocontainers and their synthesis/encapsulation technologies are systematically discussed with specific examples. Moreover, various stimulus-responsive coatings and release models of the encapsulated payloads were thoroughly analyzed. Finally, the application of the micro/nanocontainers in different fields is discussed in-depth and the prospects are put forward.

2. Classification and synthesis of micro/nanocontainers

Extrinsic self-healing coatings mainly work with the help of incorporated micro/nanocontainers. As shown in Fig. 2 that the micro/nanocontainers with high capacity can ensure the sufficient content of the encapsulated active agent content (e.g., corrosion inhibitors and healing agents). The cracks propagation causes the rupture of the containers, the healing agents flow to the cracks under the capillary action and contact with the catalysts. The polymerization of the healing agent leads to the recovery of the barrier properties of the coatings [3]. Therefore, the micro-scale containers have to be around 50–200 mm to enable easy rupture and accommodate sufficient amounts of healing agents, while the nanocontainers are more suitable for loading the corrosion inhibitors. Given the nature of the containers themselves or after the decoration of the container surface, the encapsulated payloads will spontaneously respond to the external environmental stimuli and give rapid feedback to realize the intelligent release of the loaded agents. These series of protective behaviors can be regarded as active corrosion protection and self-healing performance.

On the other hand, the design of micro/nanocontainers can avoid the direct contact between the inhibitors and coating matrix, which prevents the decline of coating integrity and ensure long-term corrosion resistance. Commonly, due to the materials category and preparation process, the micro/nanocontainers can be divided into organic, inorganic and organic/inorganic hybrid micro/nanocontainers (Fig. 3). In this section, different synthesis methods for various kinds of micro/nanocontainers are discussed in detail.

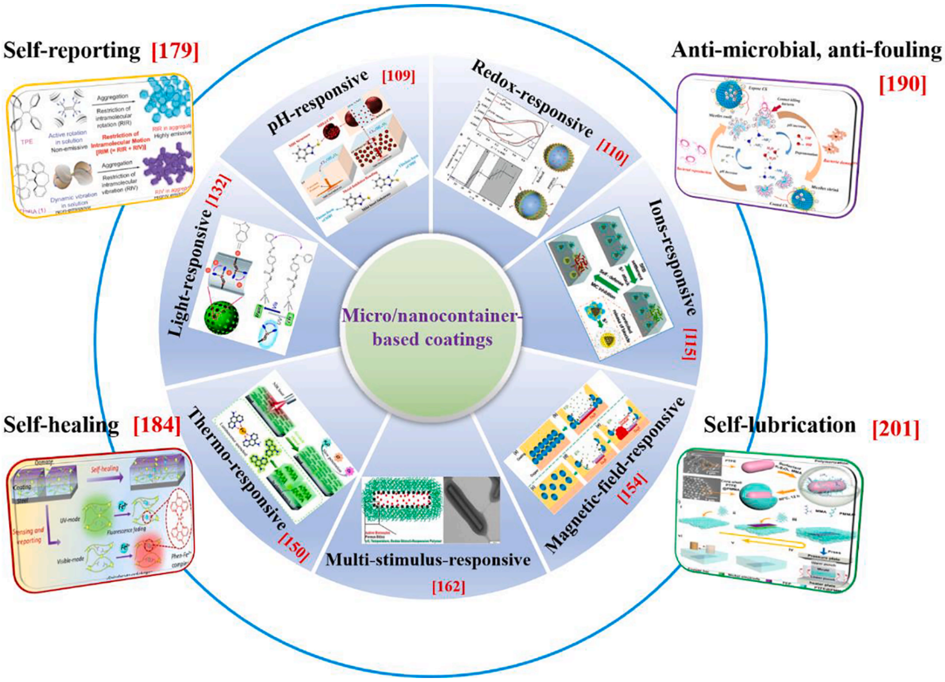

Fig. 1. Scheme of different kinds of stimulus-reponsive micro/nanocontainer-based coatings and their application in various fields. [109] Copyright 2021, [115] Copyright 2021, [154] Copyright 2018, [179] Copyright 2021, [190] Copyright 2021, [201] Copyright 2020, Reproduced with permission from Elsevier; [162] Copyright 2013, [184] Copyright 2015, Reproduced with permission from the American Chemical Society; [110] Copyright 2013, Reproduced with permission from Wiley; [132] Copyright 2015, [150] Copyright 2021, Reproduced with permission from the Royal Society of Chemistry.

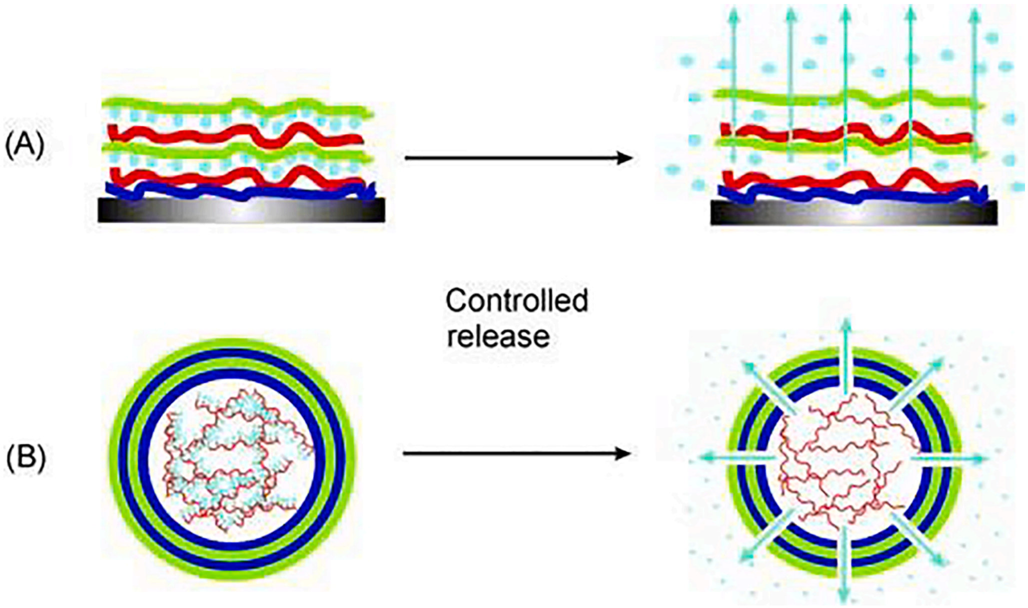

Fig. 2. Schematic diagram of the encapsulation/release of active agents. (a) active agents are embedded in the coatings; (b) active agents are encapsulated in micro/nanocontainers with a shell [4]. Copyright 2007. Reproduced with permission from Wiley.

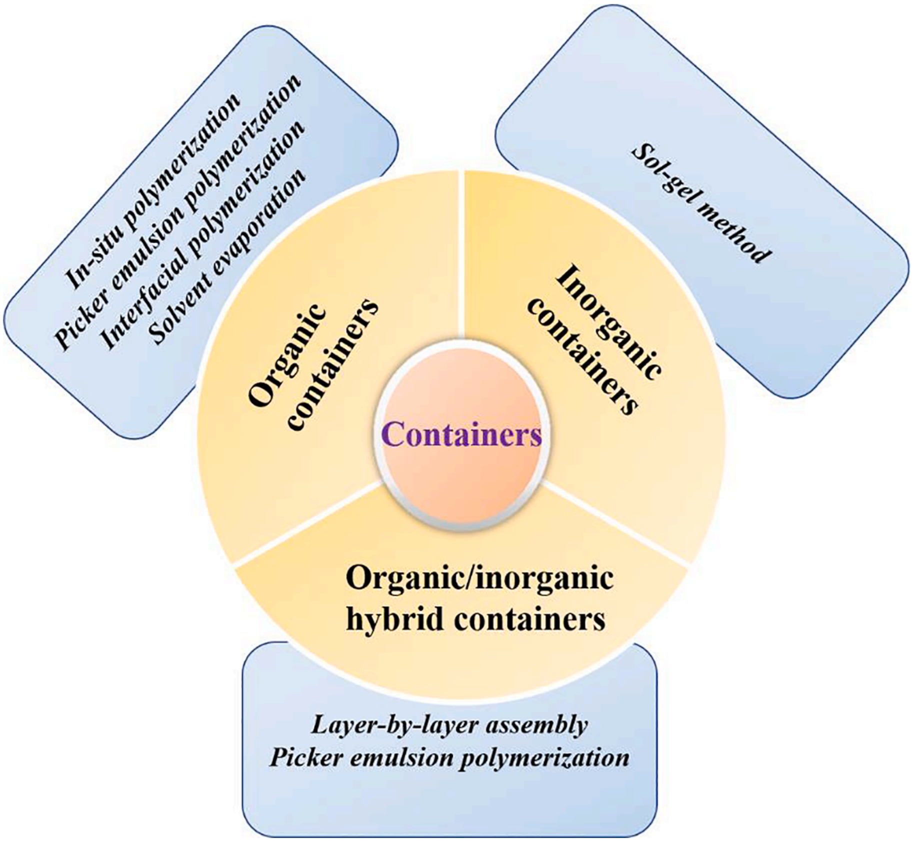

Fig. 3. Different synthesis methods for various kinds of micro/nanocontainers.

2.1. Organic micro/nanocontainers

Organic micro/nanocontainers are one of the most promising structures in self-healing materials, including microcapsules, hollow fibers, micro-network structures, etc. They can offer high load capacity, efficient protection against degradation and high compatibility with polymer matrices. The polymer shell can protect the encapsulated substance from stringent environmental factors, e.g., pH, temperature, and light, and therefore increase the service time in the corrosive environment. However, the preparation procedures of the organic micro/nanocontainers are more complicated, including polymerization reaction, encapsulation of the agent, removal of by-products and solvents, etc. The commonly used methods for preparing organic micro/nanocontainers include in-situ polymerization, Pickering emulsion polymerization, interfacial polymerization, solvent evaporation, etc.

In-situ polymerization is regarded as the most convenient and effective way among these synthesis methods, which can simultaneously realize the encapsulation of the active substances. During an in-situ polymerization process, all the reactive monomers (or soluble prepolymers) and catalysts are added into the dispersed or continuous phase, while the core material acts as the dispersed phase. Since the monomer is soluble in a single-phase and its polymer is insoluble in the emulsion system, therefore, an in-situ polymerization reaction often occurs on the dispersed phase core material surface. The monomers are pre-polymerized at the beginning of reactions. When the molecular weight or chain length of the pre-polymers gradually increases, they will deposit on the core material surface. Commonly, the in-situ polymerization has a simple and economic synthesis process, controllable size and ease of industrialization [5]. However, it usually requires a long reaction time, and the properties of the synthesized products are greatly influenced by the reaction environment, i.e. different core and shell materials, core/shell mole ratios, pH value, temperature, reaction time, type of emulsifier, stirring speed, etc.[6]. White [7] firstly prepared polymer microcapsules (size: 50–200 μm) of poly(urea–formaldehyde)-coated dicyclopentadiene repairing agent by in-situ polymerization method. The polymer capsules were pre-added with initiating monomers Grubb's catalyst to cause ring-opening for polymerization. A layer of protective film will form when the two substances interact, which will repair the microcracks on the coating surface. The repairing agent and catalyst are mixed into the coating in the form of two microcapsules to prevent direct contact with coatings. This research created a precedent in the field of microcapsules and has made great contributions to the development of container-based self-repairing systems.

Nowadays, Pickering emulsion polymerization also comes into focus as a popular strategy to form organic core–shell micro/nanocontainers. The ultrafine colloidal-sized solid particles are assembled on the water/oil interface to form a stable Pickering emulsion, then monomers are added to the continuous phase for polymerizing the micro/nanocontainers with special structures and functions [8]. In contrast to the traditional emulsion method, the application of solid particles instead of organic surface-active substances to stabilize the emulsion reaction, with low toxicity, no surfactants, low emulsifier content and adjustable droplet size [9]. On the other hand, since the Pickering emulsifier and oil phase provide different loading spaces, the micro/nanocontainers with different payloads in two separate compartments can be prepared via Pickering emulsifier polymerization. In particular, the particulate emulsifier and microcapsule shell with different stimuli responsiveness can be designed by modifying the emulsifier or selecting a specific oil phase [10]. The dual-stimuli-responsive microcontainers with multi-storage spaces for reprogrammable release functions can also be prepared through the Pickering emulsion polymerization [11]. Recently, Chen [10] modified poly-*N*-isopropylacrylamide particles with Nile Red and applied them as the Pickering emulsifier. The oil phase consisted of pH-sensitive monomers and oil-soluble fluorescent green. The as-synthesized microcapsules contained the temperature-sensitive poly-*N*-isopropylacrylamide@Nile Red shell and oil-soluble fluorescent green core (Fig. 4). Therefore, the release of the encapsulated payloads (Nile Red and oil-soluble fluorescent green) from the shell and core can be selectively under different external stimuli. The application of the multi-compartmental microcapsules with different stimulus-responsive features will show great potential in smart self-healing materials.

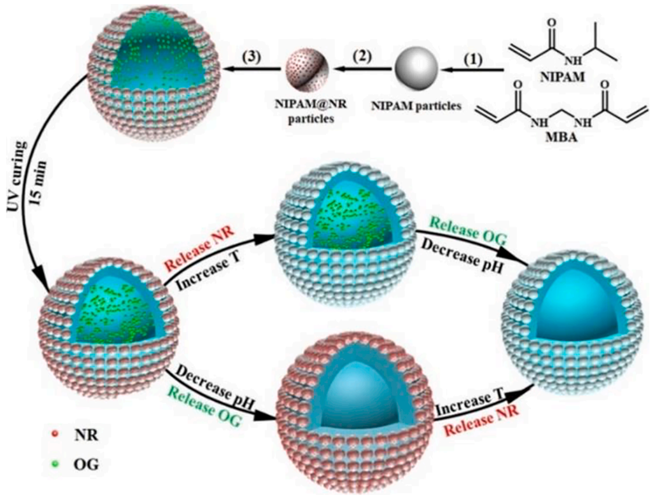

Fig. 4. Synthesis and controlled release behavior of the dual-stimuli-responsive multi-compartmental microcapsules (1) preparation of poly-*N*-isopropylacrylamide particles; (2) Nile Red loading; (3) application of the poly-*N*-isopropylacrylamide@Nile Red as the Pickering emulsifiers.[10] Copyright 2020. Reproduced with permission from the American Chemical Society.

The interfacial polymerization method is another method appropriate for the large-scale production of organic capsules. The polymerization reaction often happens at the organic-water interface between two incompatible solutions dissolved with the shell and core monomers, respectively. Finally, the capsules with encapsulated agents as the core are formed at the interface. Sun [12] loaded hexamethylene diisocyanate in the double-layered shells of microcapsules. The inner polyurea shell layer was prepared by interfacial polymerization of tetraethylenepentamine and isocyanates. The microcapsules had a diameter of 80 ± 22 μm, a shell thickness of 3.8 ± 0.2 μm, and a core fraction is 74 ± 1.3 wt%. The tetraethylenepentamine was used as a cross-linker agent to promote the formation of a higher cross-linked density shell layer. Interfacial polymerization usually shows high encapsulation efficiency, mild reaction conditions and controllable size of the microcapsules [13]. However, the selection of suitable pre-monomers and synthesis parameters are crucial for the performance of the capsules [14]. In addition, large quantities of solvents are required during the synthesis process.

The solvent evaporation method is also a common method for preparing organic capsules. The polymer shell and core materials are firstly dissolved in an organic solvent. Subsequently, the stabilizer is dropwise added to the mixed solution under continuous stirring until forming a polymer droplet containing the core materials. The shell of the containers gradually solidifies after the evaporation of the solvent and finally obtains the microcapsules. Gu [15] synthesized bisphenol A cyanate ester/polyglycidyl methyacrylate microcapsules through the solvent evaporation technique. The as-prepared microcapsules were spherical in shape with an average diameter of 31.5 μm and a wall thickness of 2.2 μm (Fig. 5). Moreover, the fabricated composite coatings with 8 wt% of the synthesized microcapsules processed excellent self-healing performance.

The size of the microcapsules can be well controlled by varying the emulsifier concentration and agitation speed during the synthesis process. Khan [16] synthesized epoxy-filled microcapsules by the solvent evaporation method. The lowest average size with the core content of 54 % was obtained when the emulsifier concentration was 8 wt% and the stirring speed was 500 rpm. Generally, the properties of the microcapsules synthesized via this method can be easily controlled by adjusting the experimental parameters (temperature, core/shell mole ratios, agitation speed, etc.). Moreover, the solvent evaporation method also shows high encapsulation efficiency and low solvent residue, which is more feasible for solid core materials [17].

Specifically, 2D convents organic framework (COF), appears as a typical representative of the new organic container, attracting much attention for designing such self-healing materials due to their flexible and porous structure, specific surface area, controllable pore size, etc. [18,19]. COFs are formed by the covalent bonding of organic elements, and their porous structure provides a channel for material permeation and also serves as a carrier for accommodating corrosion inhibitors to achieve the active corrosion protection of metal substrates [20,21]. Moreover, COFs exhibit weak interlayer interactions and thus show

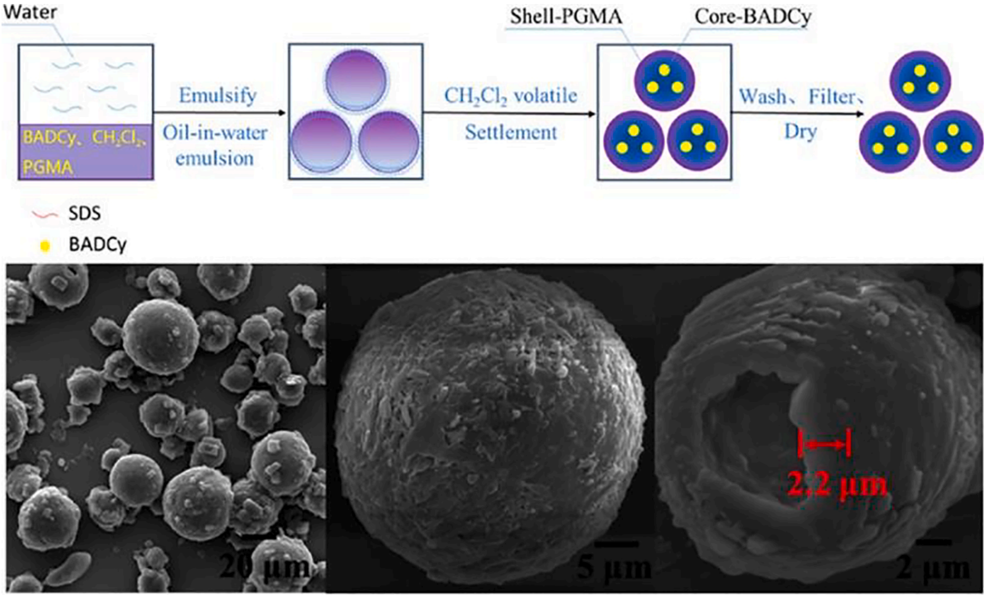

Fig. 5. Synthesis process and its morphology of bisphenol A cyanate ester/polyglycidyl methyacrylate microcapsules via solvent evaporation method.[15] Copyright 2016. Reproduced with permission from the American Chemical Society.

better compatibility and dispersion in organic matrices [22]. Liu [22] synthesized TpPa-1 (Tp: 1,3,5-Triformylphrogroglucinol, Pa-1: 1,4-phenylenediamine) COF nanocontainers by Schiff base reaction. The benzotriazole (BTA) inhibitors are loaded into the TpPa-1 nanocontainers and then embedded into the epoxy coatings. The BTA/TpPa-1 embedded epoxy coatings exhibited good corrosion resistance after 60 days, with an impedance value of $6.45 \times 10^8\ \Omega\ \mathrm{cm}^2$. In addition, the hybrid of COF-modified GO sheets as nanofillers is also investigated for further enhancing the corrosion resistance of the epoxy coatings [21,23].

Theoretically, different synthetic methods can produce organic containers of various sizes (1–1000 μm), and the diameter is greatly affected by the synthesis parameters, such as emulsifier content, agitation speed, reaction time, etc. In general, increasing the emulsifier content or agitation speeds will generate smaller-sized and narrow size distributed containers. On the other hand, the container diameter also has a significant impact on its mechanical properties, while the smaller-sized containers often suffer higher loads than the larger containers. The micro/nanocontainers will not rupture when the outer shell is robust, which cannot realize the repair effect. And the containers cannot survive in the coating matrix if they are sufficiently weak. Therefore, the selection of micro/nanocontainers with rational size and mechanical strength is beneficial to obtaining excellent self-healing performance of the smart coatings.

2.2. *Inorganic micro/nanocontainers*

Inorganic micro/nanocontainers mainly utilize their cavity structures, which can load the active agents inside the nanoparticles. After the surface modification of the nanoparticles, it can be easily achieved excellent compatibility and controlled release of the loaded active substances. The intelligent micro/nanocontainers are stimulated by a certain external microenvironment, and their structure will undergo a reversible or irreversible change. Consequently, the encapsulated functional species in the inorganic micro/nanocontainers, such as corrosion inhibitors, release into the cracked areas to inhibit further corrosion. Inorganic micro/nanocontainers usually have a small size, good stability, large coverage, and easy encapsulation process. Also, compared to the organic micro/nanocontainers, the inhibitor encapsulation process in inorganic containers is much easier, and the application of inorganic micro/nanocontainers in the coating matrix can improve the overall thermomechanical properties and barrier performance of the self-healing system even after the total release of the loaded inhibitors [24]. So far, titanium dioxide, cerium dioxide, mesoporous silica, nanoclays, halloysite nanotubes, layered double hydroxide (LDH), multi-walled carbon nanotubes, hydroxyapatite, etc. are widely investigated as inorganic containers [25–33]. The encapsulated active agent can be either inorganic inhibitors (cerium salt, molybdate, tungstate [34–36]) or organic inhibitors, such as BTA, 5-aminoindazole, 8-hydroxyquinoline (8-HQ) and L-histidine [37–40]).

However, the main drawback and limitation of the inorganic micro/nanocontainers that may hinder their development is their poor interfacial compatibility with polymer materials, which will lead to undesirable aggregation in coatings [41]. Moreover, the aggregated inorganic micro/nanocontainers will induce the formation of the micropores or micro defects, which reversely accelerate the penetration process of the aggressive ions and therefore reduce the service life. In addition, due to the special structure of the nanoparticles, the loading capacity of the active species is relatively lower when compared to other containers. Commonly, the loading capacities of the inorganic containers are generally lower than 20 %, which limits the long-term active corrosion protection applications [33,42,43]. Therefore, the improvement of the interfacial compatibility and dispersion in the polymer matrix and the enhancement of the loading capacity for the inhibitors are still imperative aspects needed to be solved.

The sol–gel method is the main approach for synthesizing inorganic micro/nano containers, which can happen at room temperature and the reaction environment is mild. The most typical example in practical application is the synthesis of mesoporous silica and titanium dioxide containers. In this method, the high chemically active component (inorganic shell material, such as tetraethoxysilane and tetrabutyl titanate) are used as precursors and dissolved in water to form low-viscosity solutions [44–46]. The emulsified droplets are obtained in vigorous stirring, which acts as a reactor for the suspension containing sol particles. However, the micro/nanocontainers obtained via this method often are not compact, which is evidenced by some visible micro-pores or defects on their surface after the drying process. Moreover, the reaction process is time-consuming and the prepared nano-sized containers show limited load capacity of active agents [13]. Stöber [47] first developed a chemical reaction that can control the growth of the spherical silica particles by the hydrolysis and condensation reactions of tetraethoxysilane under alkaline reaction conditions. The size of the as-prepared particles ranged from less than 0.05 μm to 2 μm in diameter. Following, more and more inorganic hollow spheres are synthesized as micro/nanocontainers using the sol–gel method. Wang [48] prepared hollow mesoporous zirconia nanospheres by the sol–gel method and loaded the ʟ-carnosine green corrosion inhibitors. The release of the ʟ-carnosine inhibitors was pH-sensitive, while 90 % of them are released only within 70 min when under pH 10.0. The hollow mesoporous zirconia nanospheres nanocontainers with ʟ-carnosine inhibitors were dispersed in the water-based epoxy resin coating to design a type of intelligent anti-corrosion system. The scanning vibrating electrode technique results showed that the anodic current densities of the nanocontainers-based coatings were 6.7 $\mu A\cdot cm^{-2}$ (with nanosphere diameter of 300 nm) and 10.4 $\mu A\cdot cm^{-2}$ (with nanosphere diameter of 150 nm), respectively, after 24 h of immersion, which were much smaller than that of the pure epoxy coatings (22.9 $\mu A\cdot cm^{-2}$).

Compared with the organic micro/nanocontainers, the inorganic containers usually exhibit constant shapes and stable physicochemical and mechanical properties. However, the inorganic containers have low compatibility with organic coatings and lack responsive functionality in most cases. In addition, the release mechanism of the encapsulated payloads for inorganic and organic containers shows a great difference. Commonly, the inhibitors released from organic micro/nanocontainers mainly rely on the chemical reactions on the shell wall, including the breakage of the covalent bond and depolymerization of the shell walls. In contrast, the release of the encapsulated payloads from inorganic micro/nanocontainers is more influenced by the physical or mechanical effects, such as outer pressure, thermomechanical destruction and the porosity of the micro/nanocontainer surface, etc.

2.3. *Organic/inorganic hybrid micro/nanocontainers*

Organic/inorganic hybrid micro/nanocontainers typically have a hollow lumen and a hybrid wall, which can be prepared with a combination of inorganic constituents and organic substances. Commonly, organic micro/nanocontainers usually display multi-functions and adjustable properties, but their mechanical property is weak, while inorganic micro/nanocontainers have good physiochemical stability and strong mechanical properties, but their rigid structure and inertness often limit their application range [49] The typical organic/inorganic hybrid micro/nanocontainers include inorganic nanoparticles covered layer-by-layer (LBL) polyelectrolytes [31,50,51], polymeric coated inorganic nanospheres/nanotubes [32,52], inorganic coated organic hollow nanospheres [53] and metal–organic framework (MOF) [54,55], etc.

The LBL assembly technique is an innovative method for designing two-dimensional or three-dimensional molecular structures with certain orientation and tight arrangements, which are formed with the active molecules spontaneously adsorbed on the solid–liquid or solid–gas interface [56]. Lvov [57] firstly produced a thin film through the electrostatic interaction of oppositely charged polyelectrolytes. After that, LBL technology becomes a versatile method for assembling polyelectrolyte films on multiple substrates, which can realize the precious control of the thickness, composition and molecular organization of the deposited layers [58,59]. Caruso [60] fabricated the silica-polymer hybrid capsules via the LBL assembly of polyelectrolyte and inorganic nanoparticles, which afforded a simple route for synthesizing diverse charged polymers and inorganic hybrid nanocapsules, such as Fe_3O_4, graphene oxide, Au, SnO_2 and ZnO nanoparticles [61–65]. This kind of hybrid micro/nanocontainers not only provides stable structures and physical/chemical properties but also offers multi-functions for enriching the application ranges in various fields [66,67]. Furthermore, since the nature of polyelectrolytes, the permeability of each layer can be controlled by varying the pH, ionic strength, temperature and magnetic or electromagnetic fields, therefore, the synthesized polymer-coated nanoparticles exhibit multi stimuli-responsiveness [65,68–70]. Shchukin firstly reported the LBL assembled polyelectrolyte layer to achieve the pH-triggered release of inhibitors [50]. After that, numerous works have been concentrated on the LBL assembled micro/nanocontainers for the various stimulus-responsiveness release, and their applications have also been widely used in corrosion protection, storage and delivery tool, wastewater remediation and drug delivery fields [71–73].

In addition, depositing a functional inorganic substance onto polymer capsules is also considered an alternative method for synthesizing multifunctional organic/inorganic hybrid capsules. For instance, Li [74] used graphene oxide as a Pickering emulsion stabilizer to prepare graphene oxide microcapsules coated with linseed oil. Graphene oxide microcapsules have both the physical barrier effect of graphene and microcapsules characteristics. The scratched and healed coatings with the microcapsules showed no-corrosion products after 43 h of salt spray test, exhibiting excellent corrosion inhibition and self-repairing effects. Yi [75] synthesized the microcapsules loaded with isophorone diisocyanate healing agents by the Pickering emulsion method. The resulting microcapsules were spherical with a shell thickness of 4.5 μm and an average diameter of 40–117 μm. The size of the microcapsules can also be controlled by the lignin content and the oil–water volume ratios of the Pickering emulsions. Apart from the Pickering emulsion method, Wu [76] prepared the silica/polyurea hybrid microcapsules loaded with hexamethylene diisocyanate via the combination of interfacial polymerization and the sol–gel method. The synthesized microcapsules were 57–328 μm in diameter, 1–8 μm in shell thickness and 51.2–65.6 % in the core rate. The scratched area of 5×5 cm^2 steel coated with the microcapsules-based self-healing anti-corrosion coating were almost completely rust-free after immersion in 10 wt% NaCl solution at room temperature for 48 h, confirming its great corrosion resistance.

MOF is also a representative example of organic/inorganic hybrid containers, which is flourishing in the past decade for their abundant variety, high surface area, high stability and adjustable morphology. MOFs have received numerous attention in energy storage, catalysis, drug delivery, separation membrane and electromagnetic wave shielding fields [54,77]. Zeolitic imidazolate framework (ZIF), as typical MOFs, are constructed with tetrahedral units, formed by one Zn^{2+} cation and four imidazolate anions. Especially, ZIF-8 can decompose under weakly acidic conditions and can be used as a pH-responsive container. Yang [78] reported a pH-responsive BTA@ZIF-8@tannic acid controlled-release system by precipitation polymerization from a mixed methanol solution containing BTA and zinc nitrate hexahydrate. The impedance value at 0.01 Hz was about 2 orders of magnitude higher than that of the pure epoxy coatings after 20 days of immersion. Besides, more and more active agents are loaded into ZIF-8 nanocontainers, exhibiting multi-functions for self-healing materials [55,79,80].

Combining the advantages of organic and inorganic micro/nanocontainers, the organic/inorganic hybrid micro/nanocontainers display excellent physicochemical properties and multi-responsive functions, which provides higher compatibility with both organic and inorganic coating matrices. However, the release properties of the encapsulated active payloads are also dependent on the organic components in the hybrid containers. Additionally, the dispersion of these containers, whether organic, inorganic or organic/inorganic hybrid micro/nanocontainers, is critical for achieving highly efficient self-healing performance, therefore, it is equally important to develop a convenient and effective coating technology.

In addition to the above discussion, the authors also give some typical examples of different types of stimulus-responsive micro/nanocontainers in Table 1.

3. Release kinetic of the encapsulated active agents from the micro/nanocontainers

The encapsulation of the active agents in the micro/nanocontainers can be achieved through physical or chemical interactions between the

Table 1
Examples of the different stimulus-responsive micro/nanocontainers.

Type	Micro/nanocontainers	Inhibitors/Healing agent	Trigger factors	Ref.
Organic micro/nanocontainers	poly(urea-ormaldehyde)	BTA	Mechanical/pH	[81]
	poly(urea-urethane)	2-oxoacetates	UV	[82]
	alginate hydrogel capsules	silver	Chloride ions	[83]
	calcium alginate gel capsules	imidazoline quaternary ammonium salt	Thermo	[84]
	polyaniline/poly(2,5-dimercapto-1,3,4-thiadiazole)	2,5-dimercapto-1,3,4-thiadiazole	Redox	[85]
Inorganic micro/nanocontainers	LDH	sodium molybdate	pH	[86]
	graphene	BTA	pH	[87]
	Fe_3O_4@mSiO_2	8-HQ	Redox	[88]
	mesoporous SiO_2	2-mercaptobenzothiazole (MBT)	pH/redox	[89]
	TiN@mesoporous SiO_2	BTA	NIR	[90]
	TiO_2/carbon black nanoparticles	fluorine silane	NIR/UV	[91]
Organic/inorganic hybrid micro/nanocontainers	ZIF	benzimidazole	pH	[92]
	MOF/graphene oxide	2-mercaptobenzimidazole (MBI)	pH	[93]
	SiO_2/polyelectrolyte layers	BTA	pH	[51]
	silica-poly(*N*-isopropylacrylamide)	rhodamine B	Thermo	[94]

inhibitors and carriers. When the coatings are subjected to an external stimulus and trigger the response characteristics of the micro/nanocontainer, the encapsulated inhibitors inside the containers will be released to the corrosive sites and therefore inhibit the further development of the corrosion phenomenon. However, the loading capability, dispersion status, particle size, solubility and types of corrosion inhibitors greatly affect the release kinetics of the payloads [95]. Therefore, the investigation of the release kinetics of the encapsulated inhibitors attracted much attention, which is of great importance to ensure the reliability and timeliness of the inhibitor release. However, in many cases, theoretical equations for the extended-release of corrosion inhibitors are not available, so more adequate empirical equations can be used in some cases. According to the literature reports, several release kinetic models can represent the release of corrosion inhibitors as a function of time, which is usually used to present information about the diffusion process and matrix degradation [86,96–99]. These model equations can be derived from a theoretical analysis of the process, which is listed as Eqs. (1–6). The goodness of fit can be assessed by the correlation coefficient (R^2) value.

(a) Zero-order model:

$$M_t = M_0 + k_0 t \tag{1}$$

M_t = amounts of released inhibitors at time t, M_0 = initial amounts of inhibitors, k_0 = zero-order release rate constant, t = release time. This is an ideal release method that describes the profile release that the same amount of the encapsulated active substances by a unit of time.

(b) First-order model:

$$\ln\left(\frac{M_t}{M_\infty}\right) = -k_1 t \tag{2}$$

M_∞ = amounts of released inhibitors at equilibrium, k_1 = first-order release rate constant. In this way, the graphic decimal logarithm of the release of encapsulated active substance will be linear with time, and the release amount of the encapsulated substances released by a unit of time diminish.

(c) Higuchi model:

$$M_t = K_H t^{\frac{1}{2}} \tag{3}$$

K_H is the Higuchi dissolution constant. The Higuchi diffusion process is based on Fick's law, which is associated with the square root of time. This relationship can be used to describe the dissolution of the substances in several modified release dosage forms.

(d) Hixson-Crowell model:

$$W_0^{\frac{1}{3}} - W_t^{\frac{1}{3}} = K_S t \tag{4}$$

W_0 = initial amounts of inhibitors, W_t = remaining amounts of inhibitors at time t, and K_s = constant incorporating the surface-volume relation. This model assumes that the release kinetics is controlled by erosion of the matrix surface and the encapsulated substances simultaneously dissolve as the matrix is eroded.

(e) Korsmeyer-Peppas model:

$$\frac{M_t}{M_0} = k_t t^n \tag{5}$$

k_t = release rate constant. The model is often used in the release analysis of polymeric formulations when the release mechanism is not clear or when other types of release phenomena are involved. This mathematical model, also known as the Power Law, is often used to describe the drug release of several different drug modified release dosage forms.

(f) Hopfenberg model:

$$1 - \left(1 - \frac{M_t}{M_\infty}\right)^{\frac{1}{n}} = kt \tag{6}$$

n = release exponent, k = release rate constant. This model assumes that the rate-limiting step of the encapsulated substances is the erosion of the matrix itself and that the time-dependent diffusion resistance does not have a significant effect on the erosion matrix.

In addition to the above commonly used release models, the Elovich, Baker-Lonsdale and Weibull models are also ever used to characterize the release behaviors of the encapsulated substances. Cao [100] prepared the 2-mercaptobenzothiazole @polyaniline (MBT@PANI) microspheres and studied its release behaviors. The size of the as-prepared microcapsules is 1.7 μm, and the loading amount of the MBT inhibitors was 23.5 wt%. The release tests confirmed that the MBT@PANI microcapsules showed good long-term sustainable controlled release properties in a 3.5 % NaCl solution. The release process of MBT inhibitors is divided into three stages, which sequentially followed the Elovich, first-order and zero-order kinetics. The controlled release system and release kinetics provide broad potential applications. Adsul [38] investigated the release rate kinetics of corrosion inhibitors from halloysite nanotubes in 3.5 wt% NaCl solutions at different pH values. They found that the Korsmeyer-Peppas model best fit for the release of the encapsulated inhibitors with a diffusional release coefficient is approximately 1, indicating that the diffusion mechanism followed a zero-order time-independent release. Therefore, they concluded that the reaction order did not change after the release rate reached a steady state. Similarly, Ghodke [101] investigated the release behaviors of fragrance molecules from halloysite nanocontainers at different pH conditions for 24 h. They found that the fragrance release amount was increased with the increasing pH value from 3 to 7. The release behavior of fragrance molecules from nanocontainers was fitted using the above release kinetic model. Results indicated that Korsemyer-Peppas showed the best fit ($R^2 = 0.9544$), whose release process was dependent on time and initial concentrations.

Commonly, the actual release process of the encapsulated substances usually involves multiple steps due to their different and complex physicochemical reactions, which makes it difficult to get an accurate mathematical fitting model to describe the release process accurately. Both these models listed above have their applicable conditions. In general, the Higuchi model, zero-order model and Korsmeyer-Peppas models are the most used release models with major appliances and best-describing characters [99]. Especially, the Korsmeyer-Peppas model can be a decision parameter between the Higuchi and zero-order model that reflects two limit cases during the release process. On the other hand, concerning the criteria to choose the "best-fitting model" to study the release kinetics of the encapsulated substances from the micro/nanocontainers. The R^2 value is widely used to evaluate the "fitting degree" of a model equation. However, the R^2 value usually gets greater with the addition of more model parameters, irrespective of the significance of the variable added to the model. Nowadays, when comparing models with a different number of parameters, it is proposed to use the adjusted correlation coefficient (R^2_{adjusted}) [99]:

$$R^2_{adjusted} = 1 - \frac{(n-1)}{(n-p)}(1 - R^2) \tag{7}$$

where n is the number of dissolution data points and p is the number of parameters in the model. Commonly, the R^2_{adjusted} will decrease when adding new model parameters whereas the R^2 increases or be constant, which will reflect the actual release condition of the encapsulated substances, displaying the best applicability.

Overall, the incorporation of different release kinetic models gives much information about the diffusion processes of the encapsulated inhibitors from micro/nanocontainers, as well as the detailed degradation process of the coating matrix [102]. This will help to gain insight for exploring the corrosion protection mechanisms of such smart anti-corrosive coatings, facilitating the optimization of existing corrosion protection systems and developing new systems with more sensitive controlled release behaviors.

4. Different stimulus-responsive coatings

Stimulus-responsive coatings can spontaneously respond to the environmental changes under the external stimulus factors. By adjusting their physicochemical properties, such as shape, solubility, permeability and surface wettability, the adaptation of the coatings to the corrosive environment will be greatly improved. So far, a variety of stimulus-responsive coatings were designed and applied in the fields of drug delivery, tissue engineering and sensing, etc.

In recent years, the application of smart stimulus-responsive coatings in the metal corrosion protection fields has attracted much attention. Generally, traditional anti-corrosive coatings can only block the penetration of the aggressive ions through their physical barrier effect. Once the coating is destroyed by the corrosive ions or mechanical actions, corrosive ions will penetrate the coating through the defect and finally reach the metal surface, causing the corrosion of the metal substrate and destruction of coatings. In contrast, micro/nanocontainers-based stimulus-responsive coatings can produce rapid and effective responses to external environmental stimuli (including pH, light, potential, temperature, ions, etc.). Consequently, the encapsulated functional species, such as corrosion inhibitors, release to the damaged areas and provide timely active corrosion protection to repair the micro-cracked regions and inhibit further corrosion reactions. However, the dispersion of micro/nanocontainers in the polymer matrix is also a very important issue that greatly affects anti-corrosive performance. Very often the micro/nanocontainers lead to a significant negative impact on the barrier properties of polymer coatings, especially when compatibility and agglomeration issues are not fully resolved. Moreover, the precisely controlled stimuli-responsive release behavior of the encapsulated active substances is also a great important aspect to achieve the long-term corrosion resistance and active corrosion protection ability.

4.1. pH-responsive coatings

Metal corrosion is accompanied by the dissolution and often subsequent hydrolysis process of metal ions, which results in the decrease of pH value in the micro corrosion anodic region. Meanwhile, the reduction reaction that happened in the micro-cathodic area led to a local pH increase. Therefore, pH fluctuation during the corrosion process can be regarded as a typical stimulus for the smart release of the encapsulated corrosion inhibitors from the micro/nanocontainers. At this time, the intelligent anticorrosive coating with the pH-responsive micro/nanocontainers can spontaneously sense the corrosion of the metal substrate after the coating structure is damaged, and then quickly give feedback to stimulate the protective function of the coatings and thereby inhibiting the corrosion of the metal substrate. The pH-responsive materials are currently the most widely researched materials, which have been successfully applied in intelligent anti-corrosive coatings. Polyelectrolyte molecules can act as a typical 'gatekeeper' for the micro/nanocontainers, which prevents the self-leakage of the loaded agents and also endows the pH-sensitive of micro/nanocontainers. When the corrosion happens, the increase or decrease of local pH value can deprotonate or protonate polymer molecules or accelerate their hydrolytic degradation reaction, which leads to an enhanced release amount of the encapsulated inhibitors. Shchukin [103] proposed to deposit multi-layer polyelectrolyte protective layers on the nanocontainer surface through an LBL self-assembly technology. As shown in Fig. 6, the polyelectrolyte contains a large number of functional groups, which can adjust their solubility autonomously with the response of local pH changes. Consequently, the encapsulated active substance will release on-demand under the stimulus of pH values and therefore realize the active corrosion protection of the metal substrate.

The commonly used polyelectrolyte 'gatekeeper' includes polydopamine [65], poly(sodium-4-styenesulfonate) [104], chitosan [105], polyacrylic acid [58,96], poly(allylamine hydrochloride) [106], tannic acid [107] and polyethyleneimine [108], etc. Haddadi [109] synthesized MBI@carbon hollow spheres using silica as the template (Fig. 7). The silica templates were modified with the polysaccharide shells through hydrothermal treatment. The release rate of MBI inhibitors is the highest in the solution with a pH value of 11. The pH difference in the micro-anodic and cathodic regions will lead to the protonation or deprotonation of MBI. The released MBI adsorbed on the steel surface in the forms of thione and thiolate to protect the metal from corrosion. The total impedance modulus of the coatings was higher than 9×10^9 Ω·cm^2 after 48 days of exposure to the corrosive solution, showing remarkable improvements in the corrosion resistance.

Overall, the release of the encapsulated inhibitors in the micro/nanocontainer is directly influenced by the micro-pH values during the corrosion process. The structure and properties of the micro/nanocontainers are altered with the response of the micro-pH changes, exhibiting the pH-responsiveness release of the encapsulated payloads. Despite tremendous progress had been made in designing various pH-responsive coatings, the potential limitations or challenges of these pH-responsive coatings are mainly reflected in the ranging of triggering pH values and the significant difference for different metals in various corrosive environments. The uncontrolled release under the effect of eternal pH changes will also have a negative influence on the release of the encapsulated substances. More importantly, the reversibility release of the encapsulated inhibitors only makes the coatings display a temporary self-healing effect.

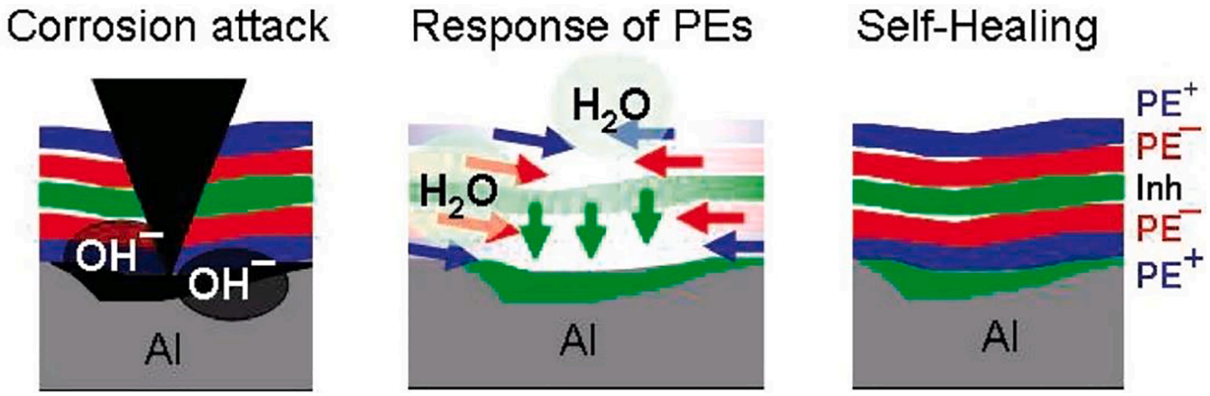

Fig. 6. Schematic diagram of self-healing mechanism for the LBL-based polyelectrolyte anti-corrosive coating. (Corrosion attacks metal surface and causes pH change of micro-zones, resulting in the pH buffer, rearrangement of the polyelectrolyte chain and release of loaded inhibitors, PE^+, PE^- represent the positively and negatively charged polyelectrolyte layer, respectively, Inh is inhibitors) [103] Copyright 2010. Reproduced with permission from the American Chemical Society.

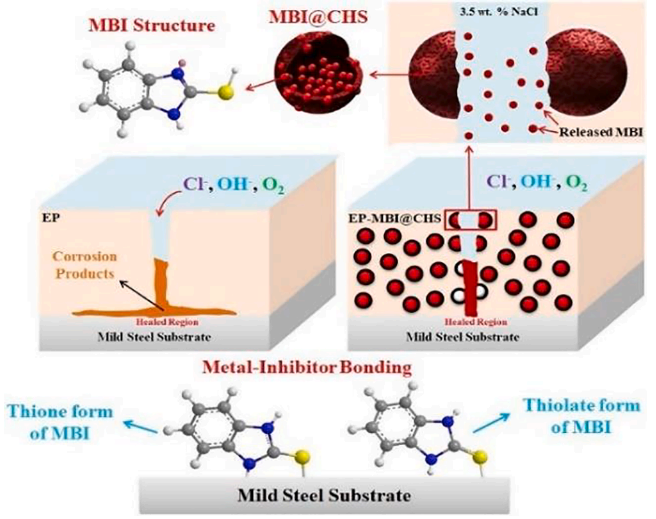

Fig. 7. Active corrosion protection mechanism of EP-MBI@carbon hollow spheres coating. (Corrosive ions damage the coating matrix and lead to the controlled release of MBI inhibitors from the broken capsules, and the deposit of the protective layer on the mild steel surface will inhibit the corrosion reactions) [109] Copyright 2021. Reproduced with permission from Elsevier.

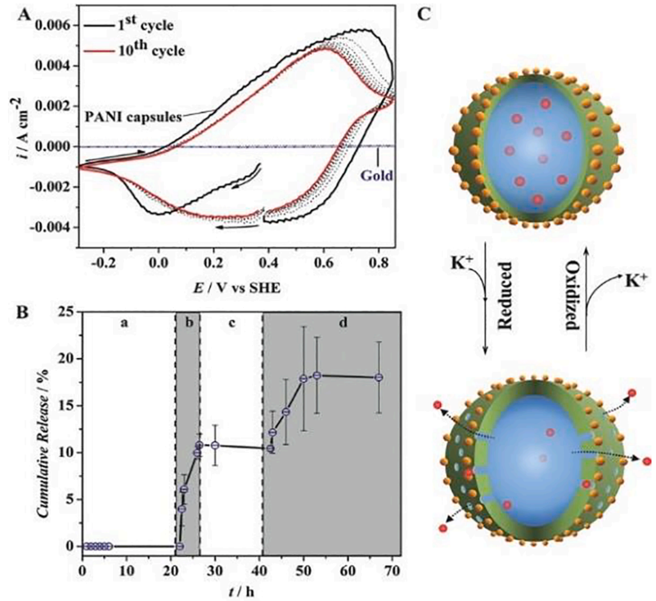

Fig. 8. (A) CV curves of PANI capsules in 0.5 M KCl solution, (B) Cumulative release of 3-NisA from PANI capsules under oxidized and reduced conditions [(a, c) white and (b, d) gray areas represent the oxidized and reduced state of PANI capsules, respectively], (C) Schematic illustration of the redox-responsive behaviors of PANI capsules (Incorporated cations in polymers cause the increase of PANI capsules volume and permeability, leading to the diffuse of the loaded 3-NisA inhibitors). [110] Copyright 2013. Reproduced with permission from Wiley.

4.2. Redox-responsive coatings

Apart from the pH changes of the micro-regions during the corrosion process, electrochemical potential fluctuation is also an important trigger for sensing the beginning of the corrosion reactions. Due to the attack of corrosive ions, local corrosion potential is reduced, which triggers the release of the encapsulated healing agents and realizes the self-healing functions. Among various redox stimulus-responsive materials, conducting polymers have attracted many interests because of their reversible redox properties. The conducting polymers can be doped with anions as the counter ions to the main chain of the oxidized polymer, which is released with the reduction of the conducting polymers. These conducting polymers show different permeability, color and solubility, etc., therefore, the changes in physicochemical properties can be used for the redox-responsive intelligence release of the encapsulated substances. Rohwerder [110] designed a self-healing coating based on the redox-sensitive PANI capsules. The PANI capsules were loaded with 3-nitrosalicylic acid (3-NisA) corrosion inhibitors (Fig. 8). CV curves confirmed the reversible redox and chemical structure characteristics of PANI capsules in corrosive environments. Moreover, the release of 3-NisA inhibitors was investigated by measuring the absorption at 225 nm with UV–vis tests under different electrochemical potentials. Different corrosion conditions were stimulated by applying electrical potentials, where the low potential simulates the corrosion initiation and the reduction of the PANI shell, the high potential represents metal passivation and reoxidation of the PANI shell by oxygen and the intact coating is stimulated without applying potentials. When no potential is applied, the PANI shell is an effective barrier to prevent the release of 3-NisA inhibitors from the core (white areas); the reduction of PANI capsules led to an increase in the PANI capsule volume and shell permeability, causing the release of the loaded inhibitors (gray areas). The re-oxidation process further led to a decrease in permeability and prevented the release process. The as-prepared PANI capsules with remarkable redox responsiveness have been successfully applied with polymeric substrates to fabricate smart anti-corrosive coatings onto zinc substrates.

Besides, the application of a kind of redox-sensitive nanovalves immobilized on the micro/nanocontainers surface also emerged as a hot topic to achieve the stimulus-responsive releases of the encapsulated agents. Such a functional delivery system usually consists of a porous inorganic or hybrid scaffold and switchable gatekeepers mounted on the micro/nanocontainers surface to open or close the pore entrances, which is used for controlling the on-demand release of the encapsulated agents [111]. These nanovalves gatekeepers often include inorganic nanoparticles, organic molecules, biological macromolecules and supramolecular assemblies, which can keep the guest molecules in the pores until they are removed by the external stimuli [112]. Accordingly, the supramolecular nanovalves installed on the micro/nanocontainers surface are the most investigated in recent years. Fu's group [113] designed the redox-trigger smart nanocontainers (RTSN) assembled by mounting supramolecular switches on the exterior mesoporous silica nanocontainer (MSN) surface (Fig. 9). The supramolecular switches underwent the reversible transition from self-complexation to self-dissociation under the redox stimuli and achieved the controlled release of the encapsulated p-coumaric acid molecules in RTSNs nanocontainers. Electrochemical tests indicated that the bilayer coating consisting of Ce(IV)-doped ZrO_2–SiO_2 sol–gel coating and RTSN incorporated ZrO_2–SiO_2 sol–gel coating exhibited the best self-healing effect, whose the low-frequency impedance value increased from 1.18×10^5 $\Omega\cdot cm^2$ to 1.51×10^6 $\Omega\cdot cm^2$ in the initial stage, then decreasing slightly and finally remaining at a stable value (2.85×10^5 $\Omega\cdot cm^2$). Based on this design, the bi-layered nanocomposite coatings displayed great potential in providing reliable and long-term active corrosion protection for aluminum alloys.

The assembled supramolecular with high binding affinity act as gatekeepers and block inhibitors within the micro/nanocontainers. Ding [88] prepared MSN with magnetic Fe_3O_4 as the core. The supramolecular nanovalves were assembled on the nanocontainer surface through the interaction of disulfide bonds (Fig. 10). The surface potential quickly dropped below −1.5 V when the Mg alloy substrate was damaged by the corrosive ions. Consequently, the disulfide bond in the nanovalve was damaged and then released the encapsulated 8-HQ inhibitors from the nanocontainers. The formation of a compact protective layer inhibited the attack of the corrosive ions. Moreover, with the help of the magnetic field, micro/nanocontainers can be uniformly dispersed close to the metal surface, which also shortened the distance between the containers and the metal surface so that the smart potential-sensitive anti-corrosive coating could exhibit a quickly self-healing function when local corrosion occurred. The intelligent coating showed a fast response and self-healing time and good corrosion resistance, which met the active corrosion protection requirement of the Mg alloys in local regions.

Apart from the supramolecular gatekeeper, quantum dots as the capping gate also received considerable attention since their easy preparation, biocompatibility, high availability, evident stimulus-responsive feature and simple modification. Sun [114] designed hollow mesoporous silica sphere nanocontainers with the redox-responsive ZnO quantum dots as nanovalves. The MBT corrosion inhibitors were loaded in the hollow mesoporous silica sphere nanocontainers and showed an on-demand release behavior under specific environments The nanovalves opened upon adding the disulfide reducing agents and caused the MBT inhibitors to release from the hollow mesoporous silica sphere. The released amount of MBT increased with the rising concentration of reducing agents, and the release amount reaches 23.4 % at 10 mM for 24 h. The constructed redox-responsive Zn-capped hollow mesoporous silica sphere nanocontainers showed promising applications for self-healing coatings, where the release is controlled by the redox environments. In addition, Li [89] embedded disulfide bonds and interaction between hollow mesoporous organosilica nanoparticles and MBT inhibitor molecules. The responsive release characteristic of MBT inhibitors under the reduction conditions were investigated in PBS (pH = 7.4) solution with different dithiothreitol concentrations. The sulfides on the exterior of nanocontainers reacted to the reduction environment and led to the breakdown of nanocontainer shells, which caused the release of the loaded MBT molecules. Electrochemical tests indicated that the corrosion of the metal substrate is greatly inhibited when the incorporated nanocontainers concentration was 1.6 $g\cdot L^{-1}$, with inhibition film resistance and charge transfer resistance values of 5.41 $k\Omega\cdot cm^2$ and 734.6 $k\Omega\cdot cm^2$, respectively. In conclusion, the embedded of nanovalves on the micro/nanocontainers surface effectively minimizes the premature release of the encapsulated agents and reduces the side effects on the coating matrix. The dynamic reversible connections, flexibility and controllability characteristics of the prepared nanovalves on the container surface promise an excellent idea for designing such an intelligent stimulus-responsive self-healing coating.

Corrosion potential is the most reliable stimulus signal during the corrosion process, which always decreases as the corrosion reaction continues. Since the uniform distribution, highly sensitive and durative corrosion potential signal, the redox-responsive self-healing coatings

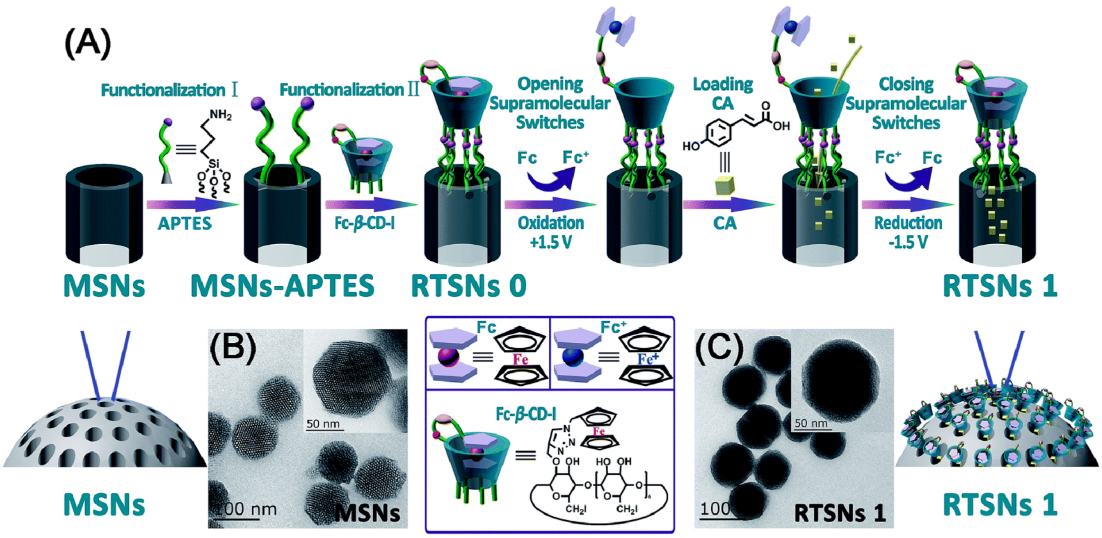

Fig. 9. (A) Schematic of the synthesis process of RTSNs 1 nanocontainers. MSNs are modified with (3-aminopropyl) trimethoxysilane and Fc-β-CD-I successively to achieve RTSNs 0. The oxidation potential is applied to open the supramolecular switches and then loaded the p-coumaric acid molecules into RTSNs 0, finally applying the reduction potential to close the switches to synthesize the RTSNs 1. (B, C) TEM image of MSNs and RTSNs 1 nanocontainers, respectively [113]. Copyright 2017. Reproduced with permission from the Royal Society of Chemistry.

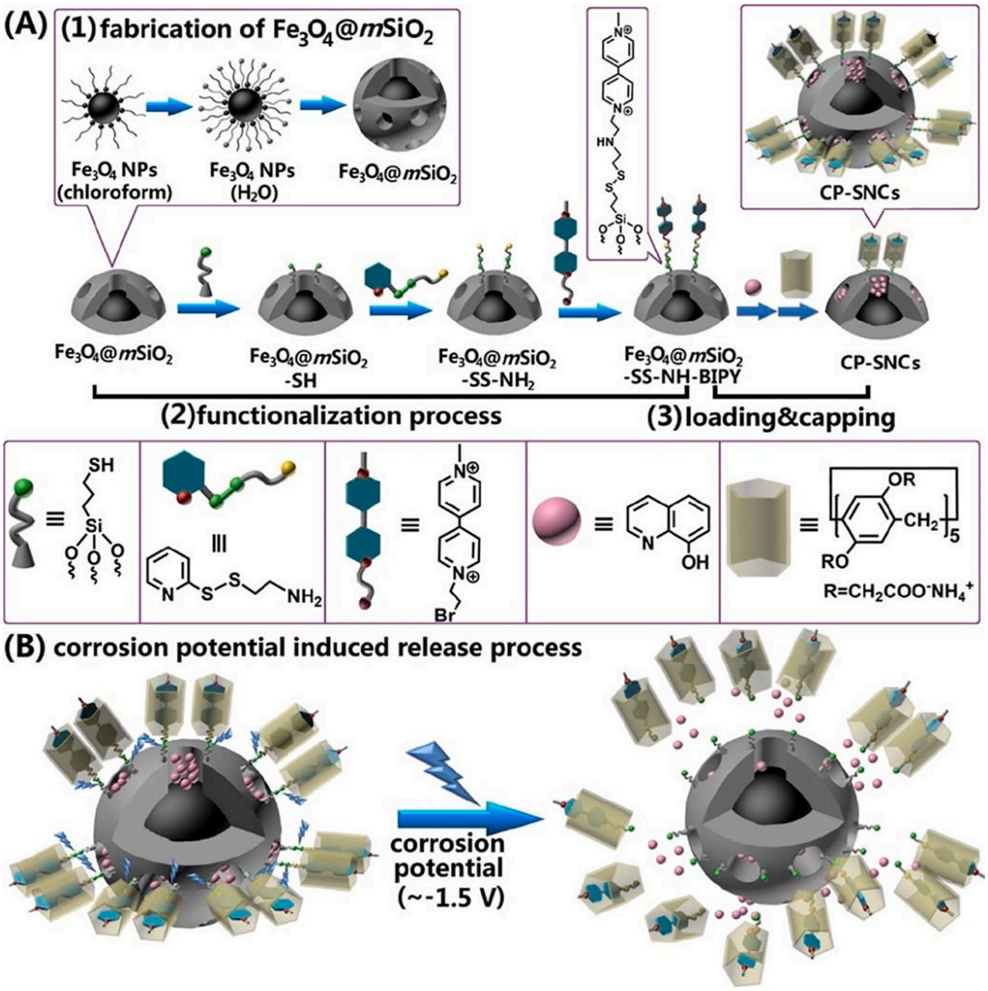

Fig. 10. Schematic of the (A) synthesis and encapsulation process of nanocontainers and (B) corrosion potential-responsive release of the encapsulated inhibitors [88]. Copyright 2017. Reproduced with permission from the American Chemical Society.

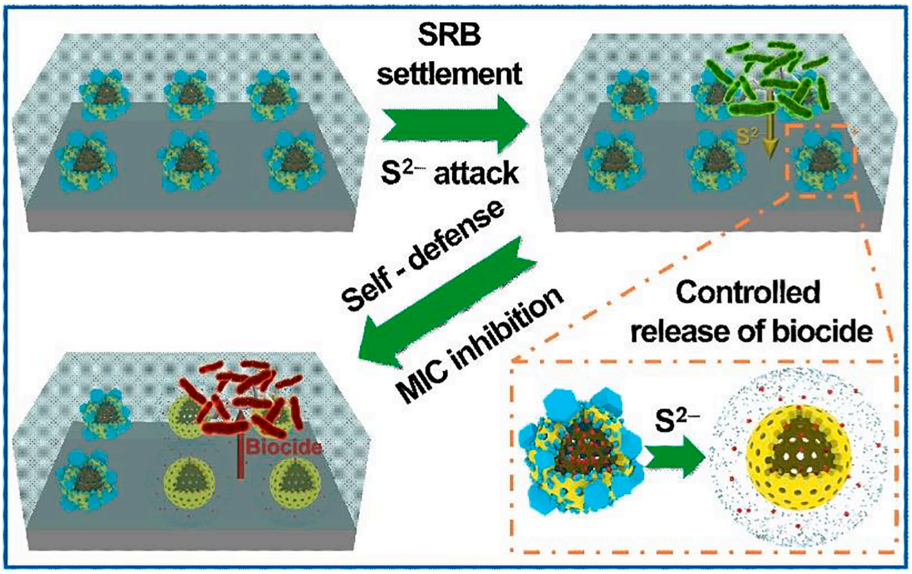

Fig. 11. Microbiological corrosion protection mechanism for the intelligent coatings (The increased S^{2-} ions concentration causes the degradation of ZIF-8, leading to the release of antibacterial agent. The released biocides permeate through the coating, kill the adhesive and corrosive microorganism and suppress the sulfate-reducing bacteria corrosion) [115] Copyright 2021. Reproduced with permission from Elsevier.

often exhibit excellent feedback and self-healing efficiency. However, the inherent limitation of these redox-responsive micro/nanocontainers is the need to have electrical contact with the metal substrate. Consequently, the dispersion of these micro/nanocontainers will also have great importance on their redox-responsiveness release. Similarly, the irreversible release of the encapsulated payloads can only provide a one-time repairing process.

4.3. *Ions-responsive coatings*

Recently, different kinds of ion-responsive micro/nanocontainers are developed, which can quickly respond to the specific aggressive ions in the corrosive environment and then release the entrapped active inhibitors to repair the cracked micro-areas on the coating surface. For instance, steel-based engineering equipment is often faced with serious microbiological corrosion when working in the marine environment containing the sulfate-reducing bacteria microorganism. Cai [115] designed a novel kind of S^{2-} ions-responsive nanocontainers by assembling ZIF-8 nanovalves on the MSN surface, while ZIF-8 acted as a gatekeeper to control the intelligent release of the loaded metronidazole inhibitors (Fig. 11). The as-prepared ZIF-8/MSN nanocontainers could respond to the S^{2-} fluctuations caused by the corrosion of sulfate-reducing bacteria. When the S^{2-} concentration was higher than 0.04 mM, the S^{2-} ions-responsive release would be achieved due to the formation of the ZnS that causes the dissolution of the ZIF-8 nanovalve. The protective performances of the smart coating with S^{2-} ions-responsive characters were evaluated in a sulfate-reducing bacteria environment. The intelligent coatings showed the highest impedance (3.31×10^7 $\Omega\cdot cm^2$) and lowest corrosion current density (1.36×10^{-10} $A\cdot cm^{-2}$) after 14 days of immersion, reflecting the excellent resistance to microbiologically influenced corrosion. This work provided a reference for designing the ions-sensitive anti-corrosive coatings and broadened their applications in the marine environment.

Besides, LDH is also a kind of typical ion-exchange material, whose chemical formula can be expressed as $[M^{2+}_{1\text{-}x}M^{3+}_{x}(OH)_2]\ [A_{x/n}{}^{n-}]\cdot mH_2O$ (M^{2+} = divalent cations, M^{3+}= trivalent cations, and A^{n-} = exchangeable charge-compensating anions). LDH has the layered structure of cations and anions, and the anions have ions exchangeability (Fig. 12). The release of anionic inhibitors entrapped in LDH can be stimulated by the corrosive anions and proceeds with the anion-exchange reactions. As a result, corrosive ions are trapped in the LDH structure while the inhibitors are released as a result of the ions-exchange process. Therefore, LDH can be regarded as a kind of ions-responsive container.

Mg-Al LDH and Zn-Al LDH are the most investigated among these LDH materials. Anjum [117] synthesized Mg-Al-based LDH coatings intercalated with 8-HQ inhibitors on AZ31 Mg alloys. The corrosive Cl^- ions are exchanged with 8-HQ inhibitors and entrapped into the LDH structure. After that, the intercalated 8-HQ was released and reacted with the Mg^{2+} ions to form an $Mg(HQ)_2$ chelate layer, which will block the active corrosive sites and seal the micro-defects (Fig. 13). Therefore, the LDH-based coatings with excellent ion-exchange capability displayed more corrosion resistance. In addition, Song [118] inserted two eco-friendly organic acid anions, aspartic acid and lauric acid, into Zn-Al LDH on AZ31 Mg alloys. The Zn-Al- lauric acid LDH has a larger $d_{(003)}$ spacing value than Zn-Al-aspartic acid LDH, showing the better adsorption ability of the Cl^- ions. Therefore, more interlayer lauric acid anions in the Zn-Al-lauric acid LDH were released and therefore significantly improve the corrosion resistance of the Mg substrate. The corrosion current density of the Zn-Al LDH (2.772×10^{-7} $A\cdot cm^{-2}$) was significantly lower than that of the bare Mg alloys (7.482×10^{-5} $A\cdot cm^{-2}$).

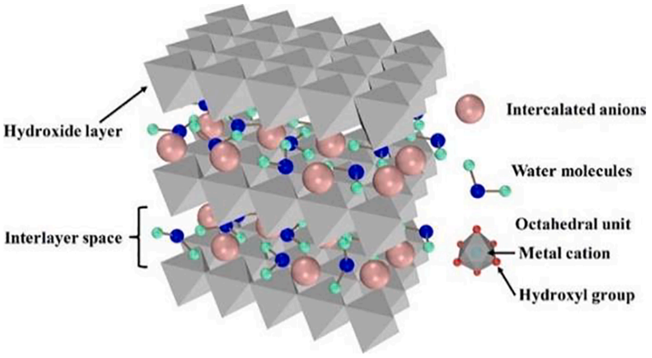

Fig. 12. Schematic of LDH structure. [116] Copyright 2018. Reproduced with permission from the American Chemical Society.

To date, lots of research are performed on designing various LDHs for the active corrosion protection of metals. Both organic and inorganic corrosion inhibitors are also intercalated into the LDHs, such as 2-mercaptobenzothiazolates, quinaldate [119], 5-aminoindazole [37], aminobenzoate [120], thiophene [121], 8-HQ [117], aliphatic carboxylates [122], phenylphosphonic acid [123], nitrate [124,125], vanadate [126], fluorine[127] etc. The entrapped inhibitors will release to inhibit the further corrosion of the metal substrate during the ions exchange process. Meanwhile, there are still some investigations that showed that the pure LDH also has a protective ability, therefore the synthetic effects of LDH and encapsulated inhibitors should be taken into consideration in such comparison studies [128,129].

In conclusion, the ions-responsive micro/nanocontainers can effectively capture the corrosives and therefore reduce the corrosion process. However, the ions-responsive process usually requires a certain corrosive environment, and many ions-responsive coatings can only respond to specific ions, which greatly limits their application ranges. In addition, the response sensitivity also needed to be improved in the following studies.

4.4. *Light-responsive coatings*

The design of light-responsive systems mainly relies on the introduction of a photosensitive group that can absorb light to trigger the photochemical reaction. In recent years, light-responsive materials have begun to be used in metal corrosion protection fields. Moreover, the electron density of the photocatalytic materials will change through UV light exposure, which provides a new photocatalysis method for controlling the corrosion protection efficiency.

The application of photocatalytic materials is a widely used method for designing such intelligent light-responsive coatings, such as TiO_2, WO_3 and CdS, et al. He [130] loaded 8-HQ inhibitors in TiO_2 nanoparticles and then coated a polyethyleneimine shell to prepare a photocatalytic self-repairing coating. The UV irradiation with 260 nm in wavelength was used to trigger the release of the 8-HQ corrosion inhibitors. Consequently, the released inhibitors form a passivation layer on the metal surface to inhibit further corrosion. Ma [90] prepared $TiN@SiO_2$ nanocontainers and loaded BTA inhibitors. The $TiN\text{-}BTA@SiO_2$ nanocontainers were integrated into a shape memory epoxy coating to prepare dual light and thermal responsive self-healing coatings (Fig. 14). The heat generation effect of TiN nanoparticles promoted the encapsulated BTA inhibitors released to the crack area within 30 s of NIR irradiation. Moreover, the photothermal effect of TiN nanoparticles also increased the surface temperature, which triggered the shape memory effect of the damaged coating to repair the scratched areas. The formation of the inhibitor-based protective layer and the sealing of the scratches will effectively inhibit the corrosion process. The coating with 2 wt% of $TiN\text{-}BTA@SiO_2$ nanocontainers maintained stable impedance values throughout the immersion time. After 15 days of immersion, the impedance (1.2×10^7 $\Omega\cdot cm^2$) was nearly 20 times higher than that of the blank epoxy coating (6.2×10^5 $\Omega\cdot cm^2$). This light-controlled self-healing method provided a reference for designing a new generation of intelligent self-healing coating with ultra-fast response time and high repair efficiency.

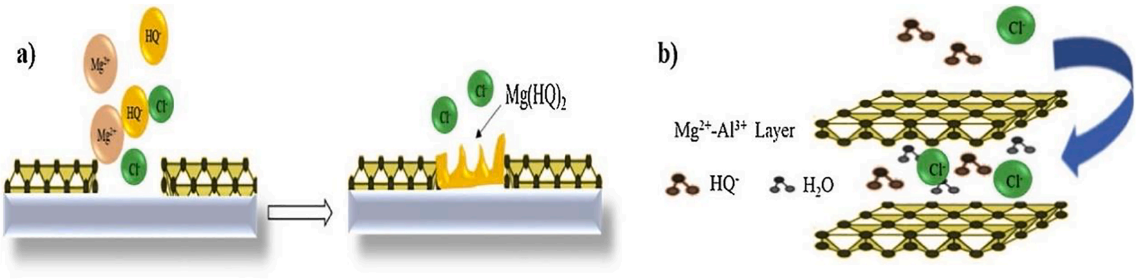

Fig. 13. Schematic diagram of the corrosion protection mechanisms for the LDH-based coatings (The intercalated ions in LDH exchange with corrosive ions, and the entrapped 8-HQ releases and interacts with Mg^{2+} ions to form chelate to block the active sites).[117] Copyright 2019. Reproduced with permission from Elsevier.

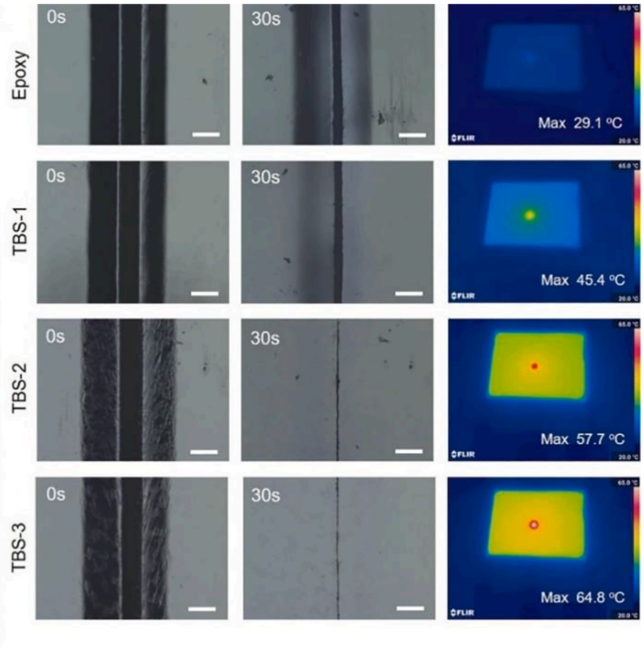

Fig. 14. The self-healing and photothermal effect of epoxy coatings with 0 wt %, 1 wt%, 2 wt% and 3 wt% TiN-BTA@mSiO$_2$ nanoparticles under NIR irradiation (TiN nanoparticles convert light energy to heat, then rapidly elevate the surface temperature and repair the scratch with the shape memory effect) [90] Copyright 2021. Reproduced with permission from Elsevier.

On the other hand, the application of photochromic molecules is also a known method. For instance, *ortho*-nitrobenzyl, coumarin, azobenzene and spiropyran-based polymers all show rapid and reversible photoisomerization [131]. Chen [132] reported a novel and simple light-triggered anti-corrosive coating by loading azobenzene molecules into MSNs. The water-borne alkyd coatings were employed to disperse the azobenzene -MSNs. The *cis* isomer of azobenzene molecules was transformed into the *trans* isomer under the visible light irradiation, which acted as a gatekeeper to prevent the diffusion of the encapsulated inhibitors. The *trans* form was converted to the *cis* form upon the UV (365 nm) light irradiation, leading to the release of azobenzene molecules. Conversely, the *cis* form was transformed to the *trans* form under the visible light at 450 nm irradiation. As a result, the pores on the MSN surface were closed and the release process was stopped (Fig. 15). The local current density tests showed that the maximum current density was constant at the noise level. Therefore, it was confirmed that the release of the encapsulated azobenzene molecules could be precisely controlled by opening or closing the surface pores, exhibiting a continuous photosensitive self-healing ability for improving the long-term protection of the underlying substrates even if the cured defect was damaged again.

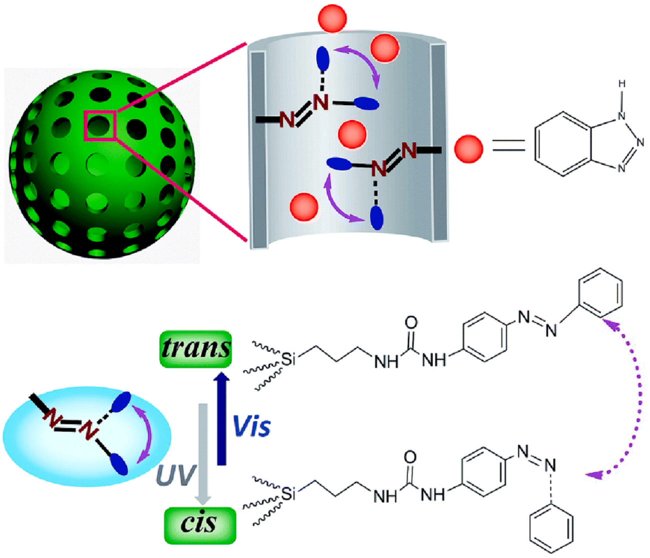

Fig. 15. Schematic diagram of the reversible release of the *trans*–*cis* photoisomerization of azobenzene molecules grafted in the MSNs. (UV irradiation at 365 nm converts azobenzene to its *cis* form, causing the pores to open, the visible light at 450 nm irradiation transforms it into the *trans* isomer and closes the pores) [132] Copyright 2015. Reproduced with permission from the Royal Society of Chemistry.

Recently, some investigations also suggest that the carbon materials, noble metal particles (silver, gold, gold sulfide or gold nanorods, etc.), Fe_3O_4, MXene and aniline black materials exhibit strong photothermal effects under light irradiation [133–138]. The light energy can be converted into heat energy upon the light illumination, affecting the structure or physicochemical properties of the polymeric shell materials. Li [91] designed a novel kind of UV-responsive microcapsules with NIR-responsive carbon nanoparticles. The nanoparticles were blended into the waterborne silicone latex together with the silica nanoparticles for preparing the self-healing superhydrophobic coatings. The loaded carbon nanoparticles generated heat to melt the microcapsules under UV irradiation and release the 1H,1H,2H,2H-perfluorooctyltriethoxysilane inhibitors inside the microcapsules. The released inhibitors migrated to the metal surface and healed the superhydrophobic property. Overall, the light stimulus is considered a prior factor among all the external stimuli sources. The light-responsive self-healing coatings can be activated remotely to repair the selected damaged areas nondestructively within an ultrafast process [139,140]. Meanwhile, the design of light-responsive micro/nanocontainers and coatings is also indispensable for the controlled release of other active agents besides in the corrosion protection fields.

4.5. Thermo-responsive coatings

As discussed above, light energy can be converted to heat energy upon light irradiation, which will release the internal energies in a short time and lead to an increase in the surface temperature. Meanwhile, as one of the most investigated stimuli factors, thermo-sensitive materials also have a wide application in corrosion protection fields. The shape memory polymer (SMP), as an emerging thermo-sensitive intelligent material, can recover to its original shape triggered by an external thermal stimulus [141]. The molecular mechanisms of the SMP are displayed in Fig. 16. SMP can be used as a coating matrix, including polyolefins, polyethers and polyesters [142], and then incorporated with different types of inhibitors or microcapsules. Especially, polyurethane is the most studied SMP material [143–146], whose thermal conversion process makes the mixed dopants melt and diffuse to the micro-defect on the coating surface. Consequently, the released healing agents will repair the cracks. However, the self-healing efficiency mainly relies on the loading and leaching capacity of the inhibitors, which can only repair the micro-defects on the coating surface.

The concept of ‘close-then-heal’ is proposed by Li’s group to improve the self-healing ability on a larger defect scale [148]. The heating process can drive the molecular chains back to a low energy state and achieve the self-closing effect with constrained shape recovery [138,149]. Then, the self-healing process in SMP can be realized at unbonded crevices by thermoplastic particles to repair the structural or macro-scale damages [90]. The detailed self-closing mechanism is shown in Fig. 17.

Based on the “close-then-heal” features, SMPs are expected to be intelligent self-healing coating. Given the photothermal conversion characteristics of graphene oxide, Cheng [150] prepared a multifunctional thermal-responsive SMP coating by incorporating polydopamine@graphene oxide loaded with 1,10-phenanthrolin-5-amine. The SMP coating showed a rapid self-healing effect within 90 s of NIR irradiation, and the formed Phen-Fe complex provided the sensing function (Fig. 18). The scratched coatings with NIR healing exhibited a higher impedance value ($4.15 \times 10^5\ \Omega\cdot cm^2$) after 15 days of immersion in 3.5 wt% NaCl solution. Therefore, the smart SMP coating exhibited excellent self-repairing performance with wide scratches as well as self-reporting function, exhibiting strong potential for actual applications.

To further enhance the healing efficiency and endow the dual-effect of the “close-then-heal” method, the thermoplastic fillers are incorporated into the SMP matrix. Huang [151] prepared new self-healing SMP coatings by incorporating microspheres containing poly(ε-caprolactone) and 8-HQ inhibitors. It was found that 10 wt% of microspheres were selected as the optimum quantity in the case of the surface morphology and barrier properties. After heating at 80 °C, the scratch was closed and recovered its corrosion resistance after heating. Then the scratch was sealed by the melted microsphere, as well as the 8-HQ inhibition effect.

The melting thermoplastic fillers usually exhibit better flow characteristics, therefore allowing the healing of larger cracks and defects, and providing better self-healing performance. Luo [152] designed the SMP coatings with thermoplastic poly(ε-caprolactone) fibers. The SMP matrix recovered its initial shape via heating, then the melting and flow of poly(ε-caprolactone) fibers connected the crack regions. In general, the close-then-heal mechanism does not damage the coating integrity and also effectively prevents the ingress of aggressive ions. Moreover, the addition of micro/nanocontainers ensures the complete sealing of the scratches and inhibits the further development of corrosion reactions. The autonomously, repeatedly and efficiently closing scheme in combination with the micro/nanocontainers technique will achieve an excellent self-healing effect at the molecular-length scale.

4.6. Magnetic-field responsive coatings

Inspired by the drug delivery system, the magnetic nanoparticles can act as drug carriers that transport to the desired area in the body, therefore it can be deduced that the magnetic-field sensitive micro/nanocontainers will show great potential in corrosion protection systems. These encapsulated active substances are released on demand and contribute to forming a protective layer on the metal surface with the response of the environmental changes, therefore achieving the active corrosion protection or self-repairing functions. However, one of the key factors affecting the coating performance is the dispersion of micro/nanocontainers in the coating matrix. The application of magnetic-based micro/nanocontainers in the coating is an improvement that can be tried since the location and orientation of the magnetic-based micro/nanocontainers can be well controlled by applying an external magnetic field. Moreover, magnetic nanoparticles show high chemical stability, lower toxicity and easy functionalization [153]. Wang [154] designed a magnetic poly(urea–formaldehyde) coating embedded with BTA inhibitors and multi-wall carbon nanotubes. As shown in Fig. 19, the magnetic microcapsules could be rapidly and easily migrated under the external magnetic field stimulus. The transmission pathway of the released BTA molecules was also shortened than that of the non-magnetic microcapsules, which extended the service time of the coatings. The electrochemical test confirmed that the inhibition efficiency of the scratched self-healing magnetic coating reach 91.2 % within 4 h of BTA releasing. Moreover, compared with the non-magnetic gradient coating, the corrosion protection efficiency of the magnetic gradient self-healing coating was improved around 6.4 times.

On the other hand, the application of magnetic-based micro/nanocontainers can also be used for corrosion detection. It was reported that aeronautical and offshore metallic structures are often affected by aggressive environments, while corrosion monitoring is more complicated and expensive. Although different types of sensors have been proposed for corrosion detection [155], only limited techniques can be used in practical corrosion processes. As generally accepted that the electric current is related to a magnetic field, therefore, the corrosion as an electrochemical process, which involves the movement of ions and electrons, should also have an associated magnetic component. Consequently, the application of the magnetic field from corrosion currents can be regarded as a possible way to monitor metal corrosion. Superconducting interference device sensors can be applied to detect corrosion in large metallic structures in aeronautical and offshore fields. However, the cost associated with the measurement and the low resolution of the initial attempts with the sensors hinders its broad applicability. Meanwhile, the magnetic flux leakage on the external part of metallic pipes can detect the gradient of induced magnetization after applying a local magnetic field [156]. One strategy to improve the sensitivity of current and magnetic flux leakage measurement is to amplify the signal of steel corrosion products by incorporating magnetic nanoparticles in the coatings [157–159]. It is known that the iron-based magnetic nanoparticles can modify their magnetic field intensity due to the changes in their surface physicochemical properties upon the pH variation, which often occurs during the corrosion process [160]. Moreover, the embedded of magnetic nanoparticles in the coating can also give a signal of physical degradation of the coating [161], thus can being an important factor to monitor corrosion activities and taking preventive measures.

4.7. Multi-stimulus-responsive coatings

Stimulus-responsive materials are widely used for the fabrication of various smart coatings and show great success in many application fields. When the smart coating works in the corrosion protection areas, it will give rapid feedback on the response of the external corrosion environment and take timely measures to achieve the active corrosion protection and self-healing effect. The current research is mainly focused on the design of a single stimulus-responsive mechanism and has made great achievements and breakthroughs. However, since the actual corrosive environment is often more complex, it is necessary to design multi stimuli-responsive coatings that adapt to various requirements in

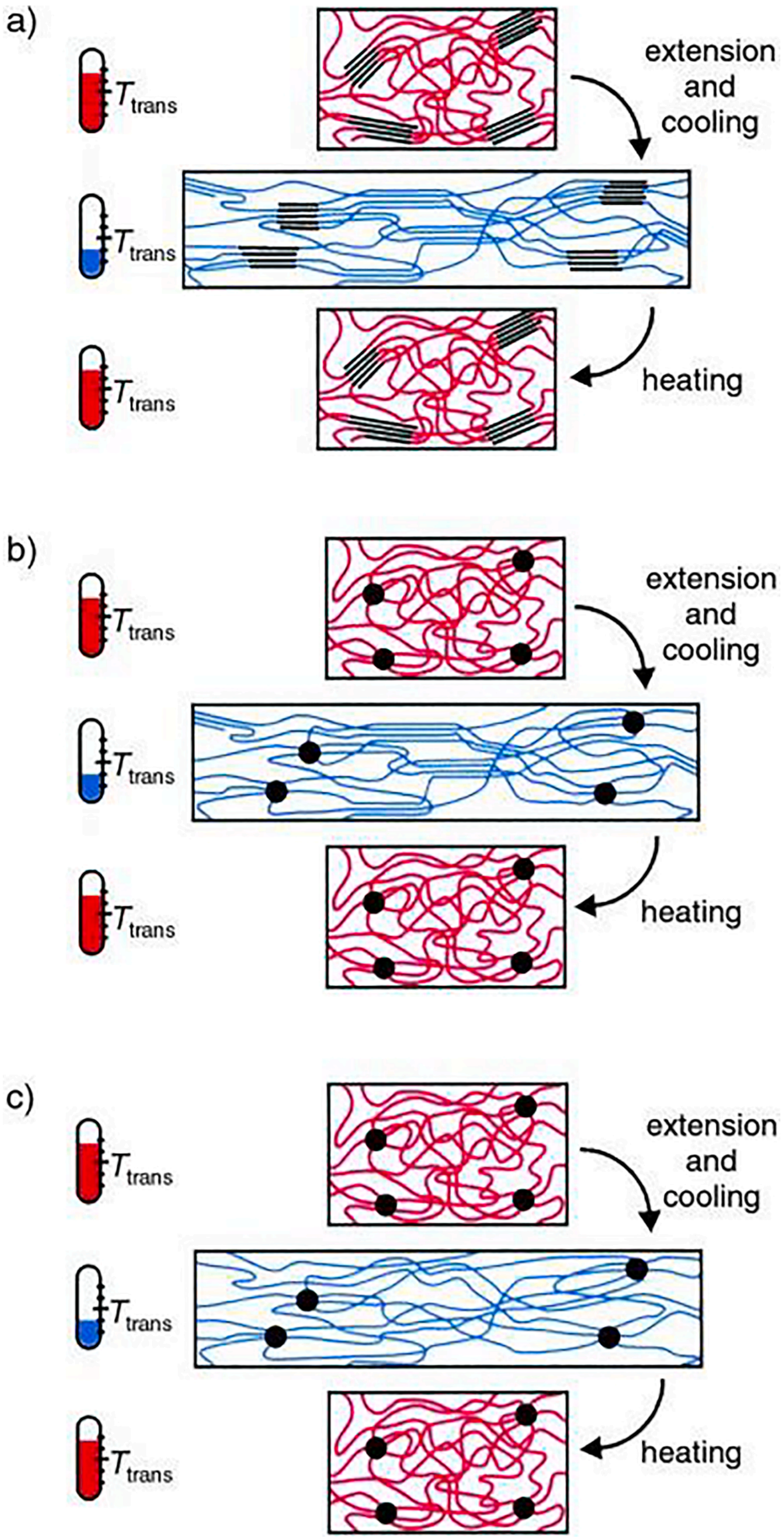

Fig. 16. The molecular mechanisms of the SMP for (a) multiblock copolymer, (b) a covalently cross-linked polymer and (c) a polymer network with $T_{trans\_}T_m$. (Black dots = net points; blue lines = molecular chains of low mobility below T_{trans}; red lines = molecular chains of high mobility above T_{trans}).[147] Copyright 2002. Reproduced with permission from Wiley.

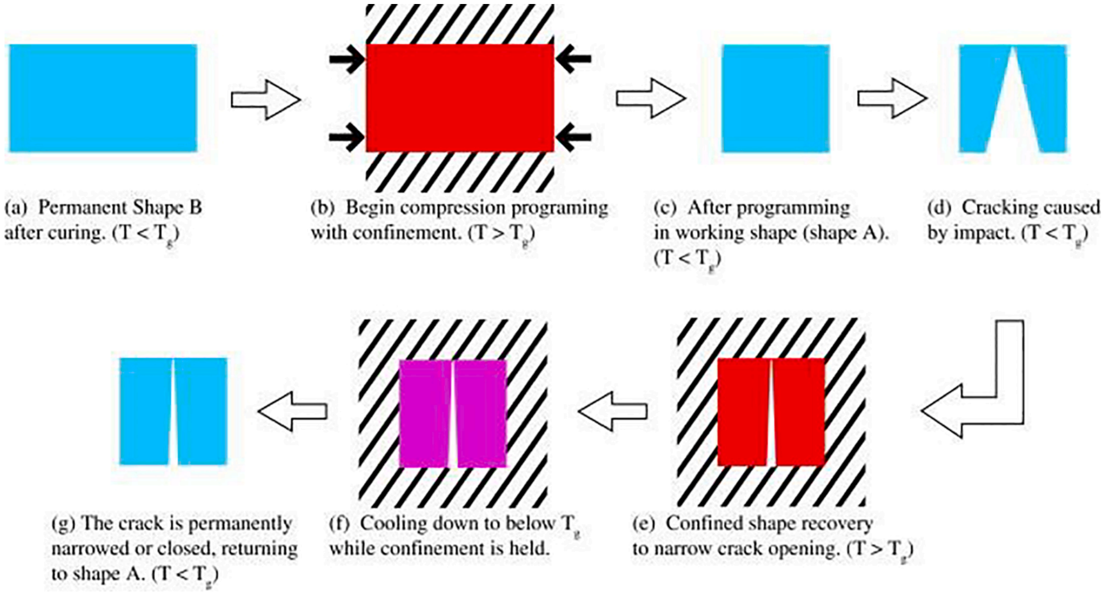

Fig. 17. The self-closing scheme of SMP. (T_g is the glass transition temperature) [148] Copyright 2010. Reproduced with permission from Elsevier.

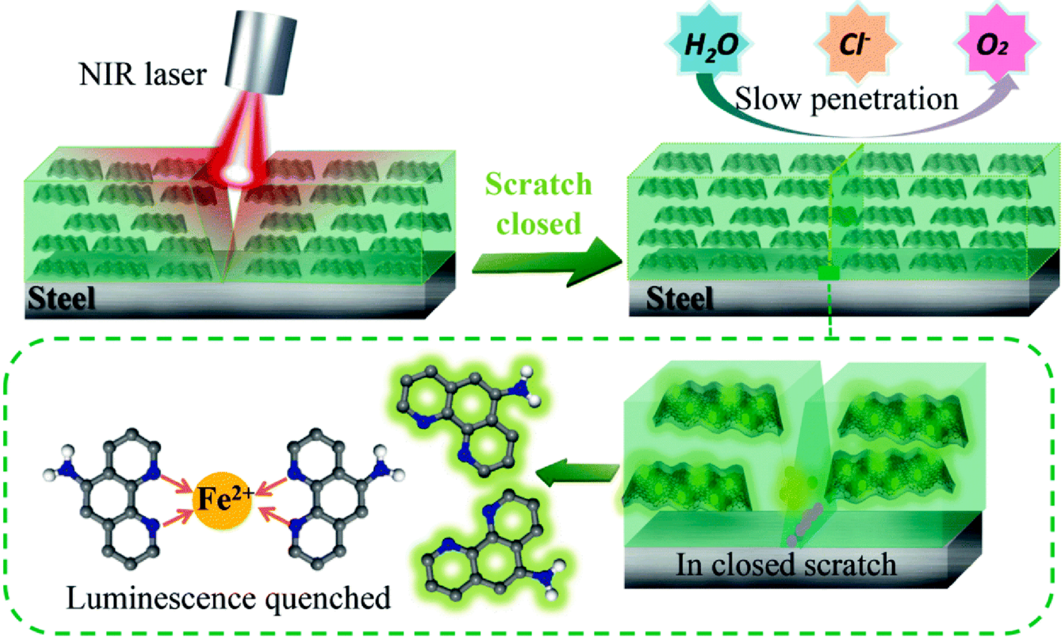

Fig. 18. Mechanism of the close-then-heal effect for self-sensing SMP coatings. (polydopamine and graphene oxide induce the shape memory effect under NIR irradiation to close the scratch, and the 1,10-phenanthrolin-5-amine enters the cracked region to achieve the self-sensing function.) [150] Copyright 2021. Reproduced with permission from the Royal Society of Chemistry.

different working environments, which is still of great importance and challenges. The design of multi-stimulus responsive coatings can respond to different triggers and selectively release the corresponding payloads inside the micro/nanocontainers, which will make the coatings more intelligent and practical. Li [162] prepared different stimulus-responsive silica/polymer double-wall hybrid nanotubes by surface grafting method. Three different polyelectrolytes, namely pH-responsive polymethacrylic acid, temperature-responsive poly-*N*-isopropylacrylamide and redox-responsive polyethylene alcohol methyl methacrylate, were deposited on the surface of silica (Fig. 20). These triple responsive nanotubes dispersed in silica-zirconia sol–gel coatings can realize a multi-response of pH, temperature and redox, exhibiting an excellent self-healing effect.

The conducting polymers are also extensively investigated due to their adjusted conductivity, environmentally friendly and anti-corrosive performance. Saremi [163] encapsulated the molybdate inhibitors in mesoporous silica. These nanocontainers were dispersed in the PPy coating. It was confirmed that the release amount of molybdate inhibitors was larger at high pH and high chlorine concentrations.

The application of a supramolecular valve is also a convenient way to realize a triple stimulus–response system, which will also make fully efficient use of inhibitors and improve the self-healing efficiency. Wang [164]. prepared acid/base/corrosion potential triple stimulus-responsive nanocontainers containing BTA corrosion inhibitors. The bistable pseudorotaxane was used as the supermolecular nanovalve to control the intelligent release of BTA inhibitors. When nanocontainers

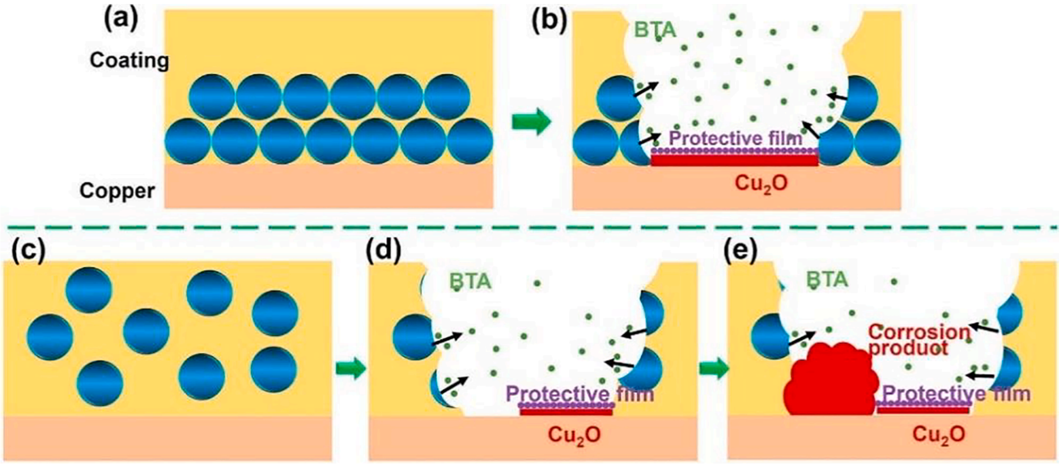

Fig. 19. Self-healing mechanism of the (a, b) self-healing magnetic gradient and (c, d, e) normal coatings. (The microcapsules in self-healing magnetic gradient coating are attracted close to the metal surface, and the released BTA inhibitors form a compact barrier film and are fully deposited on the cracked areas; while the nanocapsules in the normal coatings are evenly distributed, the cover of the protective layer will waste time, accompanied by the formation of the corrosion products on the metal surface during the inhibitors diffusion process.) [154] Copyright 2018. Reproduced with permission from Elsevier.

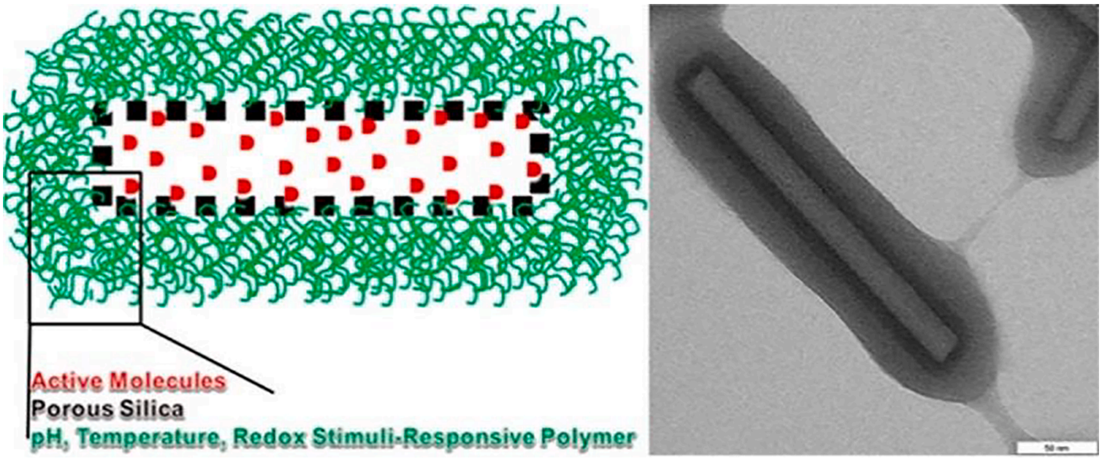

Fig. 20. Triple stimuli-responsive silica/polymer double-walled hybrid nanotubes.[162] Copyright 2013. Reproduced with permission from the American Chemical Society.

were stimulated by acid/base/corrosion potentials, the supramolecular nanovalve opened rapidly and released the loaded BTA molecules (Fig. 21). After that, the nanocontainers were added to the SiO_2-ZrO_2 sol–gel coating to design a smart self-repairing anticorrosive coating. Studies showed that the coatings could respond to both the micro pH values and corrosion potential changes during the corrosion process. The application of the supramolecular nanovalves prevented the leakage of the loaded BTA inhibitors and enhanced the response sensitivity of nanocontainers. The multi-stimulus-responsive coatings can respond to several triggering factors to deal with different environmental changes, which exhibits more intelligence and flexibility. The encapsulated payloads are released selectively under the different stimuli, featuring rapid feedback rates and superior active corrosion protection performance. It is expected that the multi-stimulus-responsive intelligent coatings will have a wider application in both industrial and daily life. In addition, the multi-stimulus-responsive behaviors of the smart coatings mainly rely on the fabrication of multi-stimulus-responsive micro/nanocontainers, whose synthesis process is usually needed multiple steps and routes are more complex. Therefore, besides developing more types of stimulus-responsive coatings, future research should also be prioritized to design a simple and effective synthesis procedure for synthesizing the multi stimuli-responsive intelligent micro/nanocontainers.

5. Application of the micro/nanocontainers in functional coatings

Nowadays, micro/nanocontainers techniques are widely used in different fields such as drug delivery, food preservation, energy storage and conversion, catalysis and metal corrosion protection [2,165–168], Commonly, the intelligent (smart) performances of coatings are reflected by the stimulus-responsive release characteristics of the loaded substances. The micro/nanocontainers give rapid feedback to the external environmental stimuli and then release the encapsulated active substances. The released agents diffuse to the micro-regions and repair the coatings. Overall, the intelligent and controlled release process of the encapsulated substances provides an active corrosion protection effect. On the other hand, the multifunctionality of the intelligent coatings mainly depends on the encapsulated active substance in the micro/nanocontainers. For example, loading fluorescent substances into the micro/nanocontainers can realize the self-reporting function, loading anti-bacterial agents can make the coating with anti-bacterial properties, etc. Herein, we discussed the self-reporting, anti-bacterial, anti-fouling and self-lubrication effects along with the self-healing coatings.

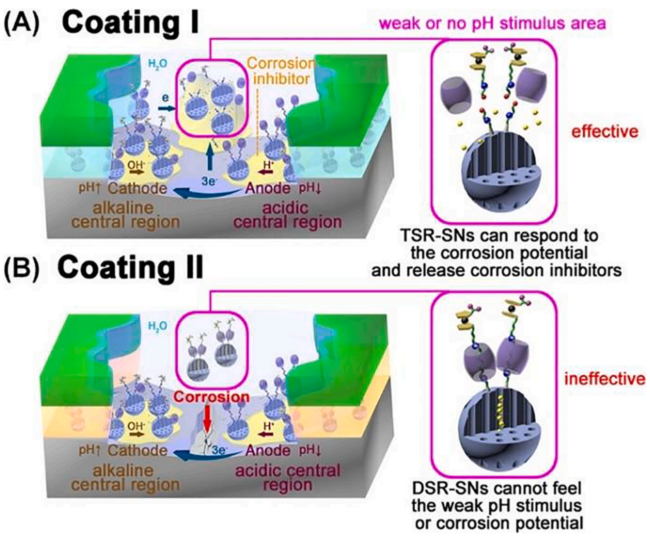

Fig. 21. Acid/alkali/corrosion potential triple stimulus-responsive coatings. (Nanocontainers give fast feedback to the corrosion potential, electrons transferring process is captured, supramolecular nanovalves are self-degraded and release the loaded inhibitors) [164] Copyright 2019. Reproduced with permission from the American Chemical Society.

5.1. Self-reporting and self-healing coatings

The application of protective coatings on the metal surface is one of the most commonly used corrosion protection strategies, which provides a physical barrier to isolate corrosive ions. However, the coating substance will gradually degrade during long-term exposure to the corrosive environment, and the structure and surface morphology of the coatings are destroyed by the aggressive species or UV. However, some micro-cracks on the coating surface are hard to detect on time, which may provide a path channel for the corrosive ions to penetrate through the coating and arrive on the metal surface, consequently accelerating the coating degradation and metal corrosion.

Recently, ‘self-reporting coatings’ are emerged for detecting micro-defects in the early corrosion process. The self-reporting function of smart coatings is often achieved by impregnating fluorescent compounds or color-changing dyes [169]. These indicators are sensitive to the corrosion-related changes, which will exhibit the fluorescence or color change with the response of local pH changes caused by the anodic or cathodic corrosion reactions, therefore playing a ‘self-reporting’ role for the smart coatings. Generally, the indicators are usually encapsulated in micro/nanocontainers to avoid the side effects of coating matrix or premature color display. At present, the synergistic effects of the self-reporting, self-protection and self-healing functions lead to a great improvement of the coating performance, presenting all-around active corrosion protection for metals. Dungen [170] encapsulated rhodamine-based fluorescent molecules in microcapsules. Nucleophilic attack of the thiol group on the 2,4-dinitrobenzenesulfonamide group led to sulfonamide chain breakage and recovery of rhodamine, resulting in a high-intensity fluorescent signal The generated bright red fluorescence on the cracked coating area exhibited the early warning effect. Apart from the rhodamine-based fluorescent, the commonly fluorescent indicators also include coumarin [171], 8-HQ [172], curcumin [173], fluorescein isothiocyanate [174], 5,6-carboxyl fluorescein [175], spiro[1H-isoindole-1,9′-[9H]xanthen]-3(2H)-one, 3′,6′-bis(diethylamino)-2-[(1-methylethylidene)amino] [176], etc. Overall, the specific complexation of fluorophores with metal ions will lead to higher sensitivity for the indication of chelation-enhanced fluorescence or chelation-enhanced quenching phenomenon, and the detected limitation of fluorescent compounds are $10^{-2} \sim 10^{-4}$ lower than those of colorimetric indicators [169]. All these advantages are beneficial for sensing corrosion in transparent or opaque coatings [176,177]. However, the incorporated fluorophores amount, encapsulation methods, etc. also have a great effect on the coating properties. The undesirable interactions between fluorescence and coating matrix may bring the fluorescence changes and damage their mechanical properties [178]. More importantly, the fluorescence in the abovementioned researches can be only observed under the UV excitation at a specific wavelength, which is inconvenient and less adaptable in the practical applications.

To make the self-reporting function more suitable for practical applications, color indicators are used in the coatings. Compared to the fluorescence, the color change that happened at the beginning of the corrosion process is easier for visual inspection. Liu [179] grafted the corrosion indicator on the polybutylene glycol skeleton. Once the coating was damaged, the reporting effect was realized through the optical color and fluorescence fading phenomenon (Fig. 22). Corrosion immersion experiments showed that the formation of the red Phen-Fe complex could play a reporting role in the early corrosion process. In addition, the smart coating exhibited a superior self-healing effect at room temperature (88 %), −20 °C (65 %) and saltwater (61 %), which can be used for the non-destructive testing and high-efficiency active self-repairing of metals.

Phenolphthalein (PhPh) is regarded as an appropriate pH indicator due to its high color contrast in the variation pH ranges. The PhPh is colorless when the pH is lower than 8.2 and turns bright pink when the pH is between 8.2 and 12 [169,180]. Galvao [181] prepared the water-based lacquer with PhPh-loaded silica nanocapsules for early corrosion detection. Moreover, the coating directly dispersed PhPh indicator is used as a comparison. The immersion test and salt spray test all showed that only the samples with encapsulated PhPh indicators could change color and indicate the corrosion process. The sample with free PhPh was unable to detect the corrosion happening, which also confirmed the necessity to encapsulate the pH indicators in nanocontainers for keeping the sensing functions of coatings. In addition, the PhPh exhibits high sensing accuracy, which is also used for sensing corrosion in the early stage. Mata [182] incorporated PhPh-loaded silica capsules into the polyethyleneimine coatings on AZ31 Mg alloys. The particles with a size below 2.2 μm were homogeneously dispersed in the polymer matrix. The immersion test showed that the pH values of the coatings changed quickly, accompanied by the appearance of pink color. The color-signal function can effectively sense the tiny corrosion activity even for the dense polyethyleneimine coatings, while the EIS test failed to detect, confirming that the nanocontainers exhibited high detection accuracy and resolution in the micron range. The pH-sensitive and color signal coatings might effectively extend the service life of coatings and reduce the maintenance costs in the daily industries.

Recently, fluorescent molecules with aggregation-induced emission (AIE) are reported to be encapsulated in micro/nanocontainers for preparing the self-reporting coatings. Due to the low concentration of the AIE fluorescent molecules in the solution, the AIE is not obvious. However, the AIE molecules are released to the damaged regions when the coating is damaged and the micro/nanocontainers rupture (Fig. 23). The AIE fluorescent molecules aggregate and exhibit fluorescence visible to the naked eye after the solvent evaporates [183]. The AIE fluorescent molecular are not subject to interference factors, which is suitable for designing the self-reporting smart coatings.

For instance, Robb [185] used the AIE-based 1,1,2,2-tetraphenylethylene as sensing agents. The mechanical damage of the coating triggered the rapid generation of a local fluorescence signal that was visible under UV light irradiation. The epoxy coatings with 10 wt% of 1,1,2,2-tetraphenylethylene microcapsules were scratched and evaluated under white and UV light irradiation. The scratch coating significantly enhanced the visual identification of damaged areas under UV light irradiation. In addition, the fluorescent area and average intensity increased proportionately with the depth of cut. Therefore, the corrosion degree of coatings could be easily measured according to the fluorescence intensity, which was beneficial for taking the corresponding

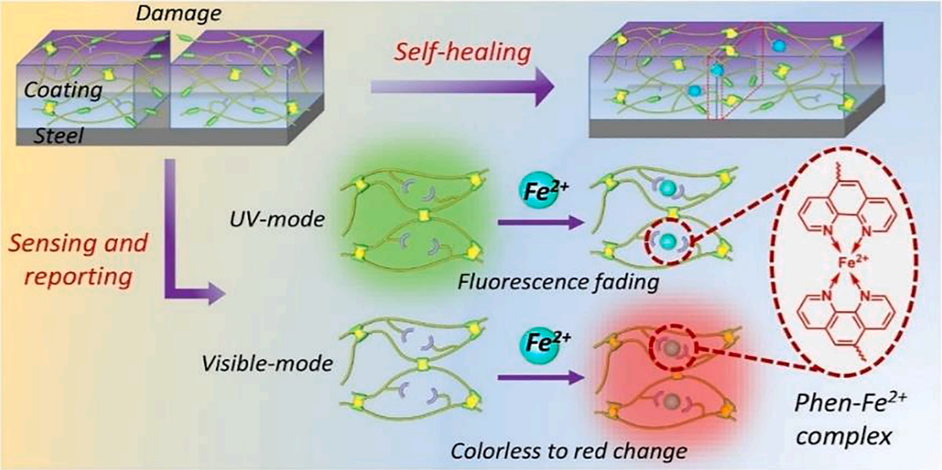

Fig. 22. Schematic of the self-healing and self-reporting mechanisms (The formation of the Phen-Fe complex displays an intense red color and fluorescence fading at the defected area, the dynamic hydrogen bonds enable the autonomous self-healing function) [179] Copyright 2021. Reproduced with permission from Elsevier.

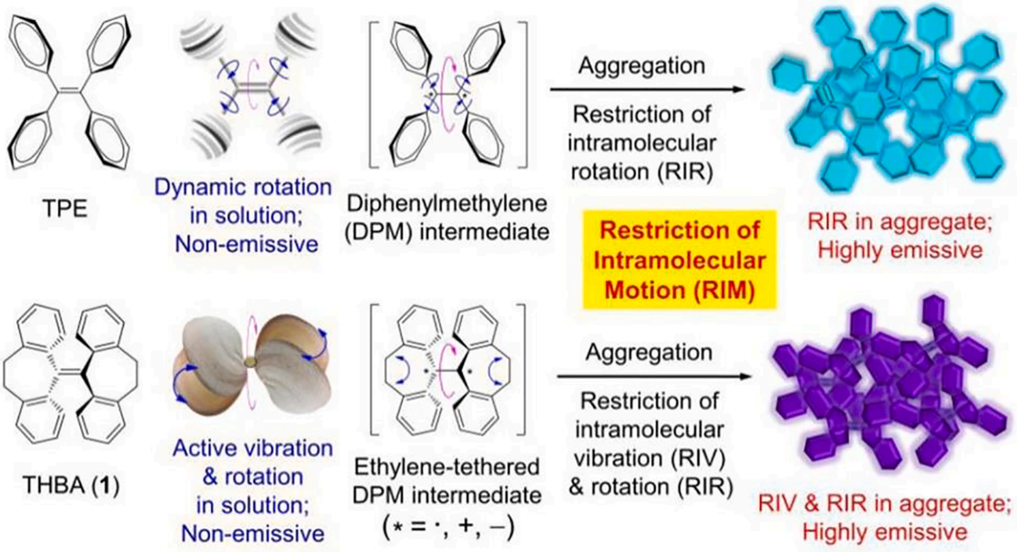

Fig. 23. AIE mechanisms with the examples of 1,1,2,2-tetraphenylethylene and shell-like luminogen of 10,10′,11,11′-tetrahydro-5,5′-bidibenzo[a,d] [7]annulenylidene [184]. Copyright 2015. Reproduced with permission from the American Chemical Society.

protection method in time. The AIE-based system with fast response and high sensitivity facilitates the design of self-reporting materials and can be used for corrosion assessment. Lee [186] used the microcapsules containing 1,1,2,2-tetraphenylethylene for the crack detection of the thiol-epoxy thermoset coating (Fig. 24). The increasing load was applied on the coating surface from 250 mN to 1000 mN through the scratch tester. Results indicated that the higher the penetration depth, the more microcapsules ruptured inside the coatings, and the blue fluorescence intensity was proportional to the number of ruptured microcapsules.

Based on the literature investigation, it can be found that the AIE-based self-reporting coatings show a simple expression mechanism, fast response time and high sensitivity and high-efficiency luminescence, which is useful for designing durable high-performance self-reporting/self-healing active corrosion protection systems. However, there are still some parameters that may affect the coating performance, such as the synthesis technology of microcapsules, incorporation amount and sensitivity of AIE molecules, etc. which still need to be further explored in future investigations.

Although a wide variety of self-reporting coatings have been designed, some fundamental limitations remain. Firstly, colored or opaque coatings should be carefully considered. The effective damage indication can only be achieved when there is a significant color contrast to the coating matrix. Secondly, enhancing the reliability and sensitivity of the indicators is also an important issue, otherwise, false alarms about the corrosion phenomenon will happen. Thirdly, the poor reversibility response of the color signal cannot provide evidence when the damage is fully repaired. Additionally, the selection of appropriate indicators in different corrosive environments, coating thickness and stability of the color signals are also important factors affecting the self-reporting performance.

5.2. *Anti-microbial and anti-fouling coatings*

Microbial corrosion in the marine environment involves many living organisms, which is one of the key factors causing the deterioration and fatigue failure of metallic structures and leading to a great economic loss every year. Therefore, endowing the anti-corrosive coatings with anti-corrosion and anti-bacterial properties is beneficial in actual industrial applications. Recently, some studies implied that the encapsulation of the anti-microbial and anti-fouling agents in the nanocapsules can

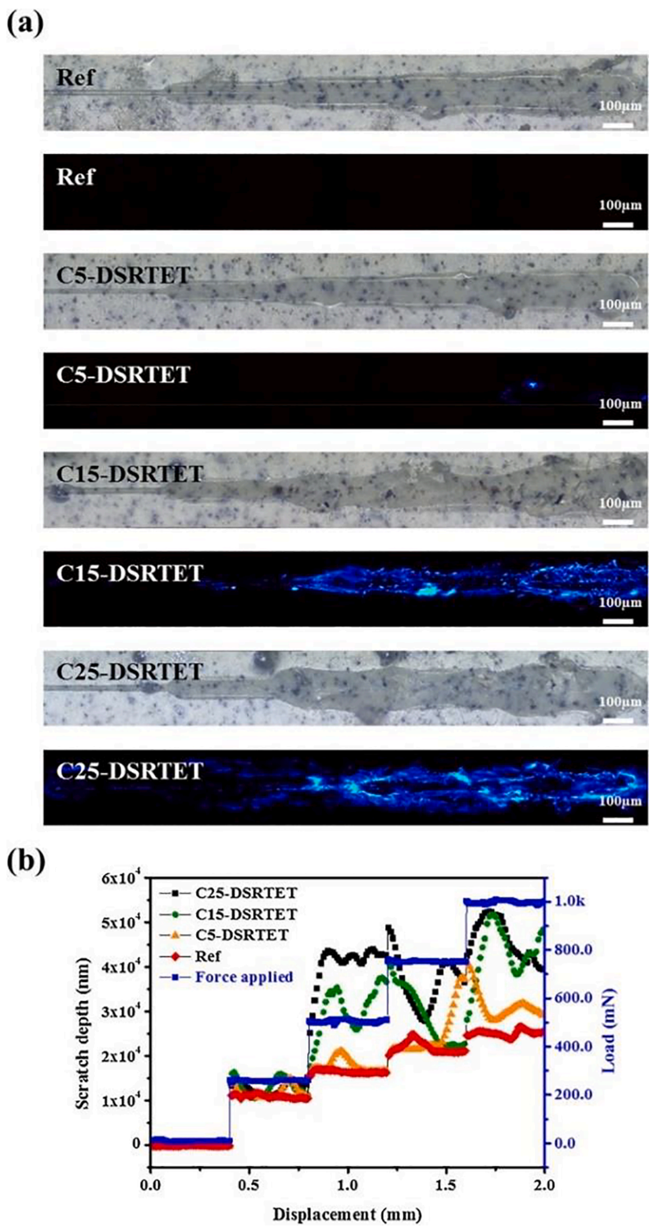

Fig. 24. Effect of microcapsules amounts on the crack sensitivity of coatings with increased load, (a) optical microscope image of the cracks under UV light and (b) the relationship between penetration depth profile and lateral position of the coatings. [186] Copyright 2018. Reproduced with permission from Elsevier.

achieve the active anti-microbial and anti-fouling functions [187]. Qian [188] prepared the microcapsules with an anti-microbial shell and anti-corrosion core by Pickering emulsion polymerization (Fig. 25). The dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride and linseed oil were encapsulated as anti-microbial and anti-corrosion agents, respectively. It was found that all the concentrations of the microcapsules exhibited anti-bacterial performances. The anti-microbial efficiency increased from 52 % (5 mg·ml^{-1}) to over 90 % (10 mg·ml^{-1}) with the increased microcapsules concentrations. However, the anti-microbial efficiency decreased to 86 % when the concentration of microcapsules was further increased to 20 mg·ml^{-1}. The anti-microbial agents killed the bacteria by interacting with the lipid bilayer structures of microbial cell membranes, which led to leakage and cell death. Overall, the microcapsules-based coatings exhibited superior self-healing and anti-microbial performances. This work was of great importance for exploring multifunctional micro/nanocontainers by encapsulating different antimicrobial or anticorrosion agents.

Biofouling is a key factor causing metal failure in seawater. Yang [189] synthesized polyurethane/ZIF-8 composite coatings with ZIF-8 nanoparticles of different sizes. It was found that the composite coating with ZIF-8 nanoparticles (~50 nm) had the highest static water contact angle (105°) and better antifouling performance with 0.51 % of algae adhesion. Moreover, the antifouling property of the composite coatings was inversely proportional to the ZIF-8 size. Especially, the anti-fouling attachment rate of the polyurethane/ZIF-8 composite coatings was 0.51 %, which was much lower than that of pure polyurethane coating (92 %).

Apart from the micro/nanocontainers, Hao [190] designed a copolymer of block chitosan *-b-* polyethylene glycol nanomicelles. The nanomicelles showed a reversible structure that responded to bacterial stimulation and was pH-sensitive (Fig. 26). The polyethylene glycol coating in an alkaline environment had a positive effect on chitosan. Due to the protonation and deprotonation reactions of amino groups in chitosan, the nanomicelles could be stimulated by bacteria to make the charge reversal and expose chitosan to kill bacteria. The zeta potential changed from $+ 15.87 \pm 0.64$ mV (alkaline) to -1.96 ± 1.09 mV (acid), and the size increased from 30 nm to 51 nm in 90 min. The chitosan-*b*-polyethylene glycol nanomicelles had reversible structural cycles in acidic/alkaline solutions, indicating the cycled stability and antibacterial properties of the nanomicelles. The anti-bacterial properties of *S. aureus* and *P. aeruginosa* were up to 97.51 % and 97.74 %, respectively. The structural design of charge-reversal micellar based on block copolymers provided a basis for exploring “non-releasing” smart anti-fouling coatings for marine applications.

Recently, environmentally friendly biological coatings have become a research hotspot. The application of natural, renewable and biodegradable polymers with anti-microbial and anti-fouling properties is an important research direction for future development. Barman [191] prepared halloysite/chitosan bio-nano composite films by loading norfloxacin drug in halloysite nanotubes through vacuum and ultrasonic treatment. The composite film showed good antibacterial properties. The continuous delivery of drugs in the composite material could be used in biomedical applications such as the wound healing field. The encapsulated natural inhibitors in the micro/nanocontainers are also effective for the active corrosion protection of metals. Mlaeto [192] prepared the bio-based anti-microbial coatings with natural phytochemical quercetin inhibitors loaded MSN. The release of flavonoid quercetin inhibitors was pH-sensitive. The anti-microbial tests showed that the coatings displayed great antibacterial properties against *Pseudomonas nitroreducens* with an enhanced zone of inhibition in the presence of MSN-quercetin-loaded coatings (Fig. 27). These kinds of environmentally friendly biological coatings have potential development prospects for anti-microbial and anti-fouling coatings.Fig. 28..

5.3. Self-lubrication coatings

Lubrication is an important part of mechanical systems, which will improve the reliability and extend the service life of the manufactured products. The research on lubricating materials has also attracted much attention. Inspired by the bionic design, composites are often endowed with self-regulating capabilities to realize the automatic lubrication effect. Typically, polyetheretherketone, poly (melamine–formaldehyde) and polysulfone are often used to prepare capsule shells and porous matrices because of their excellent formability and processability [193–195]. Guo [196] first proposed a self-lubricating composite material based on the nanocapsules in 2009. The self-lubricating materials contained poly(melamine–formaldehyde) microcapsules with a size of 100 μm, which were mechanically embedded in an epoxy resin coating. After adding 10 wt% of microcapsules, the friction coefficient and wear rate of the composite material with were reduced by 75 % and 98.3 %, respectively. The released lubricant was uniformly distributed on the

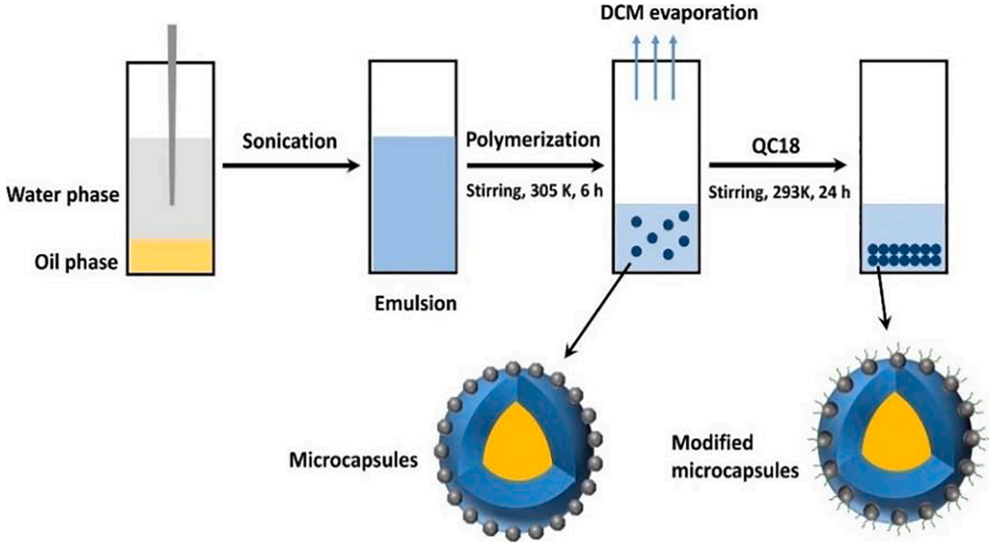

Fig. 25. Synthesis process of dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride modified microcapsules loaded with linseed oil. [188] Copyright 2020. Reproduced with permission from Elsevier.

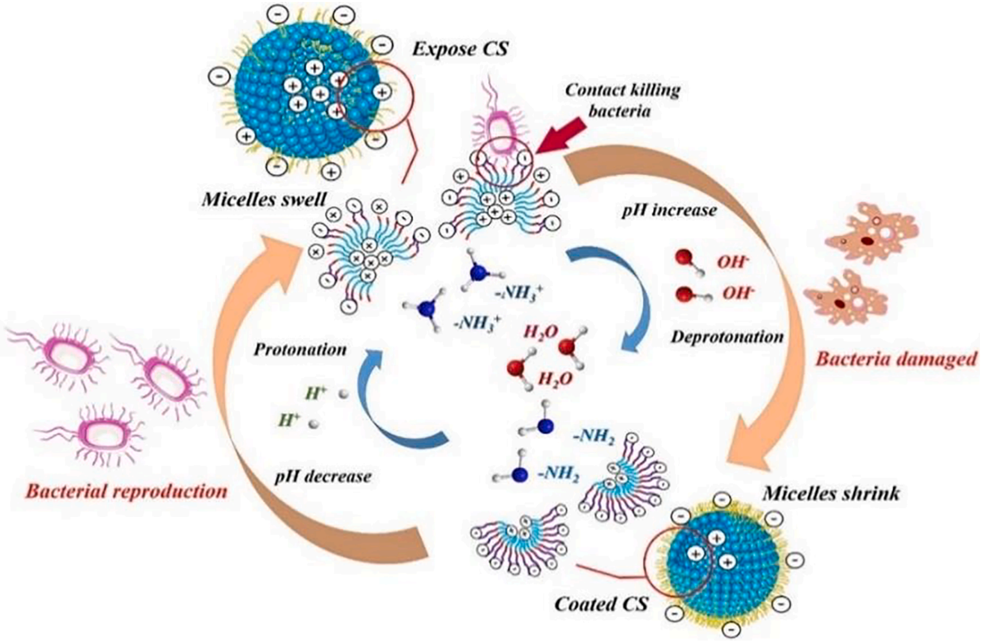

Fig. 26. The reversible structure of chitosan -*b*- polyethylene glycol nanomicelles under pH stimulus. [190] Copyright 2021. Reproduced with permission from Elsevier.

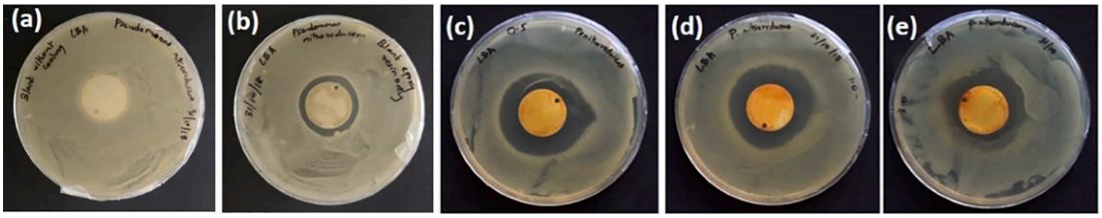

Fig. 27. The antibacterial activity of the coatings against Pseudomonas nitroreducens, (a) bare Al 6061 alloys, (b) epoxy coating, (c-e) 0.5, 1.0, 3.0 wt% MSN-quercetin loaded-coating shows the inhibition zones. [192] Copyright 2019. Reproduced with permission from Elsevier.

uneven friction surface to lubricate the interface, which improved the tribological properties of the epoxy composite. In addition, it was confirmed that the capsule size and embedded amounts also have a large effect on the mechanical properties of composite materials. Besides, incorporating the reinforcing fillers, reducing the capsule size and enhancing the interaction with the coating matrix can also greatly

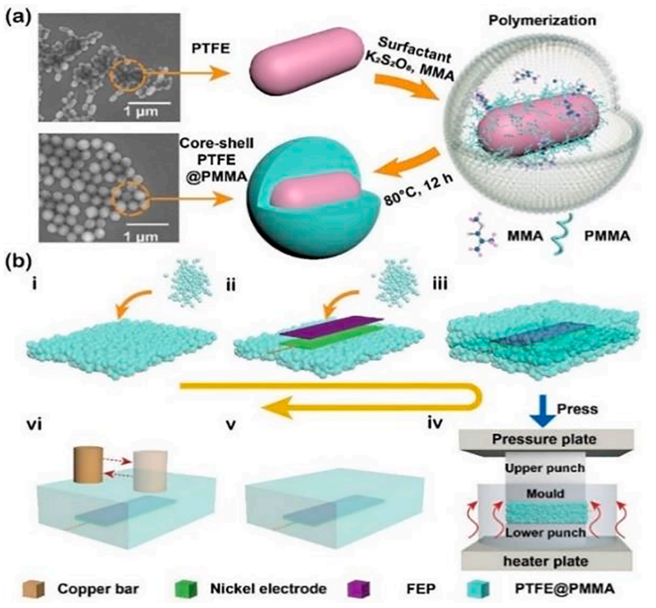

Fig. 28. (a) Synthesis procedure of polytetrafluoroethylene/polymethylmethacrylate (PEFE/PMMA) nanocapsules. (b) Schematic diagram of the (i-iii) fabrication and (iv-v) working process of the single-electrode wear sensors. [201] Copyright 2020. Reproduced with permission from Elsevier.

improve the mechanical performance of the composite coatings [197]. Therefore, developing intelligence lubricating materials with excellent mechanical behaviors was more interesting and challenging in future investigations.

On the other hand, micro/nanocontainers -based lubrication materials are often combined with other functions and endowed with more intelligence. Yan [55] incorporated amino-functionalized $Ti_3C_2T_x$ loading ZIF-8 @BTA fillers into the epoxy coating. The pH-sensitive release of BTA inhibitors from the nanocontainers formed a protective layer, thereby providing the passive and active double corrosion inhibition effects. The wear rate of the epoxy coating with the nanocontainers also decreased by one order of magnitude since the lubrication effect of $Ti_3C_2T_x$ at the friction interface and high plastic deformation resistance. In addition, the coatings displayed the lowest water absorption and the highest impedance values after 4 weeks of immersion, reflecting their long-term corrosion protection ability. On the other hand, the commonly used healing agents, such as tung oil, linseed oil and hexamethylene diisocyanate also exhibit lubricating ability, which has been encapsulated successfully into the intelligent lubricating materials with self-healing ability [198–200]. The healing agents release to the friction surface and achieve the lubrication effect, which will extend the durability and lifespans of the coatings. In addition, intelligent self-lubrication materials with self-reporting functions are also of great necessity, which will continuously monitor the lubrication status and the integrity of structures or components. Therefore, timely measures can be carried out before the material failure to avoid huge losses and security issues [201,202].

6. Conclusion and prospects

This paper gives a brief and up-to-date review of the micro/nanocontainers-based smart coatings, including the synthesis or encapsulation method of different kinds of micro/nanocontainers, release kinetic models of the encapsulated active substances and multi-triggering factors for the stimulus-responsive behavior. Numerous existing examples have been used to illustrate the feasibility of the micro/nanocontainers in smart self-healing coatings. In addition, the application of micro/nanocontainer techniques also gives more functions for smart self-healing coatings, e.g., self-reporting, anti-microbial, anti-fouling and self-lubrication functions. However, with intensive research progressing in the smart self-healing coatings, there are still some outstanding issues that needed to be adequately addressed, which are important for the future development of the smart coatings with enhanced corrosion resistance, excellent self-healing performance and multiple functions during the long-term working periods. It should be mentioned that several additional objectives should be pursued to promote the development of anticorrosion technology.

For instance, the distribution and location of micro/nanocontainers in the coating matrix is one of the greatest challenges. Moreover, the compatibility between the micro/nanocontainers and coating matrix is also needed to be further improved, the incorporation of micro/nanocontainers should neither weaken the physical properties of the coating itself nor the adhesion strength between the coating and metal substrate.

In the existing studies, the controlled release behaviors are only investigated from the micro/nanocontainers directly. However, the actual release behavior of the encapsulated inhibitors may be different when the micro/nanocontainers are embedded into the coating matrix, therefore, the actual release and diffuse behavior of the encapsulated corrosion inhibitors should be taken more seriously into consideration.

The micro/nanocontainers responding to one single stimulus are deemed insufficient since the actual corrosion environments are often complicated. Consequently, designing multi stimuli-responsive micro/nanocontainers will be more beneficial for enhancing the efficient self-healing performance and dual corrosion resistance in the actual working conditions.

Commonly, the epoxy coatings are more corrosion resistant than other coatings, therefore, the assessment time should be extended to get a more accurate understanding of the self-healing effect. In addition, developing a self-healing material with a shorter repairing time is another challenge, which will also be beneficial for extending the service time in the actual working environment.

Finally, more and more advanced environmental-friendly materials can be adapted from natural materials to obtain a broader application field. We convince that more bio-inspired self-healing coatings with multi-functions are expected to have great value for the basic research and advanced applications in 3D printing, biomedical materials, supercapacitor, sensor and flexible electronic skin fields.

Currently, the fabrication and performance evaluation of micro/nanocontainers-based self-healing coatings are mostly limited to laboratory environments. The main bottleneck for the industrial uptake of these active coatings is to explore a convenient, cost-effective and environmentally method for the large-scale procedure of micro/nanocontainers. Furthermore, systematic commercialization investigations are also necessary before the industrialization of these active self-healing coatings.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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References

[1] J. Carneiro, J. Tedim, S.C.M. Fernandes, C.S.R. Freire, A. Gandini, M.G. S. Ferreira, M.L. Zheludkevich, Functionalized chitosan-based coatings for active corrosion protection, Surf. Coat. Technol. 226 (2013) 51–59.

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

[3] D.G. Shchukin, Container-based multifunctional self-healing polymer coatings, Polym. Chem. 4 (2013) 4871.

[4] D.G. Shchukin, H. Möhwald, Self-repairing coatings containing active nanoreservoirs, Small 3 (2007) 926–943.

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

[6] S. Tzavidi, C. Zotiadis, A. Porfyris, D.M. Korres, S. Vouyiouka, Epoxy loaded poly (urea-formaldehyde) microcapsules via in situ polymerization designated for self-healing coatings, J. Appl. Polym. Sci. 137 (2020) 49323.

[7] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E. N. Brown, S. Viswanathan, Autonomic healing of polymer composites, Nature 409 (2001) 794–797.

[8] H. Zhao, Y. Yang, Y. Chen, J. Li, L. Wang, C. Li, A review of multiple Pickering emulsions: Solid stabilization, preparation, particle effect, and application, Chem. Eng. Sci. 248 (2022), 117085.

[9] H. Li, S. Li, F. Li, Z. Li, H. Wang, Fabrication of SiO$_2$ wrapped polystyrene microcapsules by Pickering polymerization for self-lubricating coatings, J. Colloid Interface Sci. 528 (2018) 92–99.

[10] Y. Chen, W. Wei, Y. Zhu, J. Luo, R. Liu, X. Liu, Synthesis of temperature/pH dual-stimuli-response multicompartmental microcapsules via pickering emulsion for preprogrammable payload release, ACS Appl. Mater. Interfaces 12 (2020) 4821–4832.

[11] Y. Cong, Q. Li, M. Chen, L. Wu, Synthesis of dual-stimuli-responsive microcontainers with two payloads in different storage spaces for preprogrammable release, Angew. Chem. 56 (2017) 3552–3556.

[12] D. Sun, Y.B. Chong, K. Chen, J. Yang, Chemically and thermally stable isocyanate microcapsules having good self-healing and self-lubricating performances, Chem. Eng. J. 346 (2018) 289–297.

[13] D.Y. Zhu, M.Z. Rong, M.Q. Zhang, Self-healing polymeric materials based on microencapsulated healing agents: From design to preparation, Prog. Polym. Sci. 49–50 (2015) 175–220.

[14] M.J.T. Raaijmakers, N.E. Benes, Current trends in interfacial polymerization chemistry, Prog. Polym. Sci. 63 (2016) 86–142.

[15] J. Gu, X. Yang, C. Li, K. Kou, Synthesis of cyanate ester microcapsules via solvent evaporation technique and its application in epoxy resins as a healing agent, Ind. Eng. Chem. Res. 55 (2016) 10941–10946.

[16] N. Islam Khan, S. Halder, S. Das, M.S. Goyat, Parametric influence towards size reduction of poly(methylmethacrylate) shelled microcapsule with epoxy core, Mater. Today. Proc. 5 (2018) 2295–2299.

[17] H. Ullah, K.A.M. Azizli, Z.B. Man, M.B.C. Ismail, M.I. Khan, The potential of microencapsulated self-healing materials for microcracks recovery in self-healing composite systems: a review, Polym. Rev. 56 (2016) 429–485.

[18] W. Li, X. Zhang, C. Zhang, M. Yu, J. Ren, W. Wang, S. Chen, Exploring the corrosion resistance of epoxy coated steel by integrating mechanochemical synthesized 2D covalent organic framework, Prog. Org. Coat. 157 (2021), 106299.

[19] X. Feng, X. Ding, D. Jiang, Covalent organic frameworks, Chem. Soc. Rev. 41 (2012) 6010–6022.

[20] C. Wang, Z. Li, J. Chen, Z. Li, Y. Yin, L. Cao, Y. Zhong, H. Wu, Covalent organic framework modified polyamide nanofiltration membrane with enhanced performance for desalination, J. Membr. Sci. 523 (2017) 273–281.

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

[22] T. Liu, W. Li, C. Zhang, W. Wang, W. Dou, S. Chen, Preparation of highly efficient self-healing anticorrosion epoxy coating by integration of benzotriazole corrosion inhibitor loaded 2D-COF, J. Ind. Eng. Chem. 97 (2021) 560–573.

[23] M. Zhang, X. Yu, Y. Lin, J. Liu, J. Wang, Anti-corrosion coatings with active and passive protective performances based on v-COF/GO nanocontainers, Prog. Org. Coat. 159 (2021), 106415.

[24] C., liu,, L., Cheng,, L., Cui,, B., Qian,, R., Zeng,, Corrosion self-diagnosing and self-repairing polymeric coatings based on zeolitic imidazolate framework decorated hydroxyapatite nanocontainer on steel, Chem. Eng. J. 431 (2022), 133476.

[25] Z. Chen, W. Yang, X. Yin, Y. Chen, Y. Liu, B. Xu, Corrosion protection of 304 stainless steel from a smart conducting polypyrrole coating doped with pH-sensitive molybdate-loaded TiO$_2$ nanocontainers, Prog. Org. Coat. 146 (2020), 105750.

[26] S. Gu, H. Shi, C. Zhang, W. Wang, F. Liu, E.-H. Han, Mesoporous CeO$_2$ containers in water-borne epoxy coatings for dual active corrosion protection of mild steel, Prog. Org. Coat. 158 (2021), 106376.

[27] G. Chen, S. Wen, J. Ma, Z. Sun, C. Lin, Z. Yue, J.M.C. Mol, M. Liu, Optimization of intrinsic self-healing silicone coatings by benzotriazole loaded mesoporous silica, Surf. Coat. Technol. 421 (2021), 127388.

[28] S.H. Adsul, K.R.C. Soma Raju, B.V. Sarada, S.H. Sonawane, R. Subasri, Evaluation of self-healing properties of inhibitor loaded nanoclay-based anticorrosive coatings on magnesium alloy AZ91D, J. Magnesium Alloys 6 (2018) 299–308.

[29] D.G. Shchukin, K.A. Yasakau, M.L. Zheludkevich, M.G.S. Ferreira, H. Möhwald, Active anticorrosion coatings with halloysite nanocontainers, J. Phys. Chem. C 112 (2008) 958–964.

[30] J. Tedim, S.K. Poznyak, A. Kuznetsova, D. Raps, T. Hack, M.L. Zheludkevich, M. G. Ferreira, Enhancement of active corrosion protection via combination of inhibitor-loaded nanocontainers, ACS Appl. Mater. Interfaces 2 (2010) 1528–1535.

[31] D.G. Shchukin, H. Möhwald, Surface-engineered nanocontainers for entrapment of corrosion inhibitors, Adv. Funct. Mater. 17 (2007) 1451–1458.

[32] P. Najmi, N. Keshmiri, M. Ramezanzadeh, B. Ramezanzadeh, Synthesis and application of Zn-doped polyaniline modified multi-walled carbon nanotubes as stimuli-responsive nanocarrier in the epoxy matrix for achieving excellent barrier-self-healing corrosion protection potency, Chem. Eng. J. 412 (2021), 128637.

[33] L. Cheng, C. Liu, H. Wu, H. Zhao, L. Wang, A two-dimensional nanocontainer based on mesoporous polydopamine coated lamellar hydroxyapatite towards anticorrosion reinforcement of waterborne epoxy coatings, Corros. Sci. 193 (2021), 109891.

[34] S.A. Haddadi, S. Hu, S. Ghaderi, A. Ghanbari, M. Ahmadipour, S.Y. Pung, S. Li, M. Feilizadeh, M. Arjmand, Amino-functionalized MXene nanosheets doped with Ce(III) as potent nanocontainers toward self-healing epoxy nanocomposite coating for corrosion protection of mild steel, ACS Appl. Mater. Interfaces 13 (2021) 42074–42093.

[35] P. Xie, Y. He, F. Zhong, C. Zhang, C. Chen, H. Li, Y. Liu, Y. Bai, J. Chen, Cu-BTA complexes coated layered double hydroxide for controlled release of corrosion inhibitors in dual self-healing waterborne epoxy coatings, Prog. Org. Coat. 153 (2021), 106164.

[36] M.J. Anjum, J.M. Zhao, V.Z. Asl, M.U. Malik, G. Yasin, W.Q. Khan, Green corrosion inhibitors intercalated Mg: Al layered double hydroxide coatings to protect Mg alloy, Rare Met. 40 (2020) 2254–2265.

[37] L. Ma, Y. Qiang, W. Zhao, Designing novel organic inhibitor loaded MgAl-LDHs nanocontainer for enhanced corrosion resistance, Chem. Eng. J. 408 (2021), 127367.

[38] S.H. Adsul, U.D. Bagale, S.H. Sonawane, R. Subasri, Release rate kinetics of corrosion inhibitor loaded halloysite nanotube-based anticorrosion coatings on magnesium alloy AZ91D, J. Magnesium Alloys 9 (2021) 202–215.

[39] A.C. Balaskas, I.A. Kartsonakis, L.A. Tziveleka, G.C. Kordas, Improvement of anti-corrosive properties of epoxy-coated AA 2024–T3 with TiO$_2$ nanocontainers loaded with 8-hydroxyquinoline, Prog. Org. Coat. 74 (2012) 418–426.

[40] A. Dehghani, G. Bahlakeh, B. Ramezanzadeh, A.H.J. Mofidabadi, Improvement of the anti-corrosion ability of a silane film with β-cyclodextrin-based nanocontainer loaded with L-histidine: Coupled experimental and simulations studies, Prog. Org. Coat. 157 (2021), 106288.

[41] X. Sheng, R. Mo, Y. Ma, X. Zhang, L. Zhang, H. Wu, Waterborne epoxy resin/polydopamine modified zirconium phosphate nanocomposite for anticorrosive coating, Ind. Eng. Chem. Res. 58 (2019) 16571–16580.

[42] J. Ding, H. Zhao, Z. Shao, H. Yu, Bioinspired smart anticorrosive coatings with an emergency-response closing function, ACS Appl. Mater. Interfaces 11 (2019) 42646–42653.

[43] A. Khan, A. Hassanein, S. Habib, M. Nawaz, R.A. Shakoor, R. Kahraman, Hybrid halloysite nanotubes as smart carriers for corrosion protection, ACS Appl. Mater. Interfaces 12 (2020) 37571–37584.

[44] M.R. Mahmoudian, Y. Alias, W.J. Basirun, M. Ebadi, Effects of different polypyrrole/TiO$_2$ nanocomposite morphologies in polyvinyl butyral coatings for preventing the corrosion of mild steel, Appl. Surf. Sci. 268 (2013) 302–311.

[45] N. Wang, W. Fu, J. Zhang, X. Li, Q. Fang, Corrosion performance of waterborne epoxy coatings containing polyethylenimine treated mesoporous-TiO$_2$ nanoparticles on mild steel, Prog. Org. Coat. 89 (2015) 114–122.

[46] J. Lin, P. Li, H. Xu, Y. Kim, Z. Jing, D. Zheng, Controlled synthesis of mesoporous single-crystalline TiO$_2$ nanoparticles for efficient photocatalytic H$_2$ evolution, J. Hazard. Mater. 391 (2020), 122530.

[47] A.F. Werner Stöber, Controlled growth of monodisperse silica spheres in the micron size range, J. Colloid Interface Sci. 26 (1968) 62–69.

[48] M. Wang, M. Liu, J. Fu, An intelligent anticorrosion coating based on pH-responsive smart nanocontainers fabricated via a facile method for protection of carbon steel, J. Mater. Chem. A 3 (2015) 6423–6431.

[49] J. Shi, Y. Jiang, X. Wang, H. Wu, D. Yang, F. Pan, Y. Su, Z. Jiang, Design and synthesis of organic-inorganic hybrid capsules for biotechnological applications, Chem. Soc. Rev. 43 (2014) 5192–5210.

[50] D.G. Shchukin, M.L. Zheludkevich, K. Yasakau, S. Lamaka, M.G.S. Ferreira, H. Möhwald, Layer-by-layer assembled nanocontainers for self-healing corrosion protection, Adv. Mater. 18 (2006) 1672–1678.

[51] M.L. Zheludkevich, D.G. Shchukin, H. Möhwald, M.G.S. Ferreira, Anticorrosion coatings with self-healing effect based on nanocontainers impregnated with corrosion inhibitor, Chem. Mater. 19 (2007) 402–411.

[52] M. Rui, Y. Jiang, A. Zhu, Sub-micron calcium carbonate as a template for the preparation of dendrite-like PANI/CNT nanocomposites and its corrosion protection properties, Chem. Eng. J. 385 (2020), 123396.

[53] I.A. Kartsonakis, G. Kordas, Synthesis and characterization of cerium molybdate nanocontainers and their inhibitor complexes, J. Am. Ceram. Soc. 93 (2010) 65–73.

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

[55] H. Yan, X. Fan, M. Cai, S. Song, M. Zhu, Amino-functionalized $Ti_3C_2T_x$ loading ZIF-8 nanocontainer@benzotriazole as multifunctional composite filler towards self-healing epoxy coating, J. Colloid Interface Sci. 602 (2021) 131–145.

[56] Q. Mo, G. Qin, K. Ling, X. Lv, N. Wang, W. Li, Layer-by-layer self-assembled polyurea layers onto MAO surface for enhancing corrosion protection to aluminum alloy 6063, Surf. Coat. Technol. 405 (2021), 126653.

[57] Y. Lvov, G. Decher, H. Möhwald, Assembly, structural characterization, and thermal behavior of layer-by-layer deposited ultrathin films of poly(vinyl sulfate) and poly(allylamine), Langmuir 9 (1993) 481–486.

[58] H.K. Singh, K.V. Yeole, S.T. Mhaske, Synthesis and characterization of layer-by-layer assembled magnesium zinc molybdate nanocontainer for anticorrosive application, Chem. Eng. J. 295 (2016) 414–426.

[59] M.D. Yilmaz, Layer-by-layer hyaluronic acid/chitosan polyelectrolyte coated mesoporous silica nanoparticles as pH-responsive nanocontainers for optical bleaching of cellulose fabrics, Carbohydr. Polym. 146 (2016) 174–180.

[60] F. Caruso, H. Möhwald, Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating, Science 282 (1998) 1111–1114.

[61] M. Izadi, T. Shahrabi, B. Ramezanzadeh, Synthesis and characterization of an advanced layer-by-layer assembled Fe_3O_4/polyaniline nanoreservoir filled with Nettle extract as a green corrosion protective system, J. Ind. Eng. Chem. 57 (2018) 263–274.

[62] N.N. Taheri, B. Ramezanzadeh, M. Mahdavian, Application of layer-by-layer assembled graphene oxide nanosheets/polyaniline/zinc cations for construction of an effective epoxy coating anti-corrosion system, J. Alloy. Compd. 800 (2019) 532–549.

[63] J. Heo, M. Choi, D. Choi, H. Jeong, H.Y. Kim, H. Jeon, S.W. Kang, J. Hong, Spray-assisted layer-by-layer self-assembly of tertiary-amine-stabilized gold nanoparticles and graphene oxide for efficient CO_2 capture, J. Membr. Sci. 601 (2020), 117905.

[64] K. Kamburova, N. Boshkova, N. Boshkov, T. Radeva, Composite coatings with polymeric modified ZnO nanoparticles and nanocontainers with inhibitor for corrosion protection of low carbon steel, Colloids Surf., A 609 (2021), 125741.

[65] Z. Chen, W. Yang, Y. Chen, X. Yin, Y. Liu, Smart coatings embedded with polydopamine-decorated layer-by-layer assembled SnO_2 nanocontainers for the corrosion protection of 304 stainless steels, J. Colloid Interface Sci. 579 (2020) 741–753.

[66] S. Donatan, A. Yashchenok, N. Khan, B. Parakhonskiy, M. Cocquyt, B. E. Pinchasik, D. Khalenkow, H. Möhwald, M. Konrad, A. Skirtach, Loading capacity versus enzyme activity in anisotropic and spherical calcium carbonate microparticles, ACS Appl. Mater. Interfaces 8 (2016) 14284–14292.

[67] Y. Ping, J. Guo, H. Ejima, X. Chen, J.J. Richardson, H. Sun, F. Caruso, pH-responsive capsules engineered from metal-phenolic networks for anticancer drug delivery, Small 11 (2015) 2032–2036.

[68] E. Marin, C. Tapeinos, S. Lauciello, G. Ciofani, J.R. Sarasua, A. Larranaga, Encapsulation of manganese dioxide nanoparticles into layer-by-layer polymer capsules for the fabrication of antioxidant microreactors, Mater. Sci. Eng. C Mater. Biol. Appl. 117 (2020), 111349.

[69] M. Barak, A.S. Aghdam, E.B.S. Ozbulut, S. Unal, F.Ç. Cebeci, Layer-by-layer assembly of nanofilms from colloidally stable amine-functionalized silica nanoparticles, Colloids Surf., A 630 (2021), 127615.

[70] X. Zhang, J. Yi, G. Zhao, L. Huang, G. Yan, Y. Chen, P. Liu, Layer-by-layer assembly of silver nanoparticles embedded polyelectrolyte multilayer on magnesium alloy with enhanced antibacterial property, Surf. Coat. Technol. 286 (2016) 103–112.

[71] Q.U.A. Nadeem, R. Gill, D.W.F. Cheung, D.G. Shchukin, Ensnaring animate-inanimate toxins using ZnO–MgO@Elastomer thin films with self-cleaning and regenerative properties, Environ. Technol. Innov. 24 (2021), 102011.

[72] E.M. Shchukina, D.G. Shchukin, Layer-by-layer coated emulsion microparticles as storage and delivery tool, Curr. Opin. Colloid Interface Sci. 17 (2012) 281–289.

[73] D. Grigoriev, E. Shchukina, D.G. Shchukin, Nanocontainers for self-healing coatings, Adv. Mater. Interfaces 4 (2017) 1600318.

[74] J. Li, Q. Feng, J. Cui, Q. Yuan, H. Qiu, S. Gao, J. Yang, Self-assembled graphene oxide microcapsules in Pickering emulsions for self-healing waterborne polyurethane coatings, Compos. Sci. Technol. 151 (2017) 282–290.

[75] H. Yi, Y. Yang, X. Gu, J. Huang, C. Wang, Multilayer composite microcapsules synthesized by Pickering emulsion templates and their application in self-healing coating, J. Mater. Chem. A 3 (2015) 13749–13757.

[76] G. Wu, J. An, D. Sun, X. Tang, Y. Xiang, J. Yang, Robust microcapsules with polyurea/silica hybrid shell for one-part self-healing anticorrosion coatings, J. Mater. Chem. A 2 (2014) 11614–11620.

[77] C. Zhou, Z. Li, J. Li, T. Yuan, B. Chen, X. Ma, D. Jiang, X. Luo, D. Chen, Y. Liu, Epoxy composite coating with excellent anticorrosion and self-healing performances based on multifunctional zeolitic imidazolate framework derived nanocontainers, Chem. Eng. J. 385 (2020), 123835.

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

[79] H. Wang, Y. Fan, L. Tian, J. Zhao, L. Ren, Colorimetric/fluorescent dual channel sensitive coating for early detection of copper alloy corrosion, Mater. Lett. 265 (2020), 127419.

[80] R.M. Abdelhameed, E. Alzahrani, A.A. Shaltout, H.E. Emam, Temperature-controlled-release of essential oil via reusable mesoporous composite of microcrystalline cellulose and zeolitic imidazole frameworks, J. Ind. Eng. Chem. 94 (2021) 134–144.

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

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

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

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

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

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

[87] C. Liu, Z. Jin, H. Zhao, L. Wang, Triple-action smart nanocontainers enhanced protective coatings with superior active and passive properties, Prog. Org. Coat. 148 (2020), 105887.

[88] C. Ding, J. Xu, L. Tong, G. Gong, W. Jiang, J. Fu, 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 9 (2017) 21034–21047.

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

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

[91] W. Li, X. Ni, X. Zhang, Y. Lei, J. Guo, J. Jin, B. You, UV-NIR dual-responsive nanocomposite coatings with healable, superhydrophobic, and contaminant-resistant properties, ACS Appl. Mater. Interfaces 12 (2020) 48101–48108.

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

[93] H. Li, Y. Qiang, W. Zhao, S. Zhang, 2-Mercaptobenzimidazole-inbuilt metal-organic-frameworks modified graphene oxide towards intelligent and excellent anti-corrosion coating, Corros. Sci. 191 (2021), 109715.

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

[95] B.A. Bhanvase, M.A. Patel, S.H. Sonawane, Kinetic properties of layer-by-layer assembled cerium zinc molybdate nanocontainers during corrosion inhibition, Corros. Sci. 88 (2014) 170–177.

[96] S.E. Karekar, U.D. Bagale, S.H. Sonawane, B.A. Bhanvase, D.V. Pinjari, A smart coating established with encapsulation of Zinc Molybdate centred nanocontainer for active corrosion protection of mild steel: release kinetics of corrosion inhibitor, Compos. Interfaces 25 (2018) 785–808.

[97] D. Yu, J. Wang, W. Hu, R. Guo, Preparation and controlled release behavior of halloysite/2-mercaptobenzothiazole nanocomposite with calcined halloysite as nanocontainer, Mater. Des. 129 (2017) 103–110.

[98] H.P. Lim, C.W. Ooi, B.T. Tey, E.S. Chan, Controlled delivery of oral insulin aspart using pH-responsive alginate/κ-carrageenan composite hydrogel beads, React. Funct. Polym. 120 (2017) 20–29.

[99] P. Costa, Modeling and comparison of dissolution profiles, Eur. J. Pharm. Sci. 13 (2001) 123–133.

[100] Y. Cao, X. Yuan, X. Wang, W. Li, H. Yang, Synthesis and controlled release kinetics of pH-sensitive hollow polyaniline microspheres encapsuled with the corrosion inhibitor, J. Mol. Liq. 342 (2021), 117497.

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

[102] M. Tyagi, B.A. Bhanvase, S.L. Pandharipande, Computational studies on release of corrosion inhibitor from layer-by-layer assembled silica nanocontainer, Ind. Eng. Chem. Res. 53 (2014) 9764–9771.

[103] D.V. Andreeva, E.V. Skorb, D.G. Shchukin, Layer-by-layer polyelectrolyte/inhibitor nanostructures for metal corrosion protection, ACS Appl. Mater. Interfaces 2 (2010) 1954–1962.

[104] X. Liu, C. Gu, Z. Wen, B. Hou, Improvement of active corrosion protection of carbon steel by water-based epoxy coating with smart CeO_2 nanocontainers, Prog. Org. Coat. 115 (2018) 195–204.

[105] A.B.M. da Cunha, D.A. Leal, L.R.L. Santos, I.C. Riegel-Vidotti, C.E.B. Marino, pH-sensitive microcapsules based on biopolymers for active corrosion protection of carbon steel at different pH, Surf. Coat. Technol. 402 (2020), 126338.

[106] J. Carneiro, A.F. Caetano, A. Kuznetsova, F. Maia, A.N. Salak, J. Tedim, N. Scharnagl, M.L. Zheludkevich, M.G.S. Ferreira, Polyelectrolyte-modified layered double hydroxide nanocontainers as vehicles for combined inhibitors, RSC Adv. 5 (2015) 39916–39929.

[107] M. Allais, F. Meyer, V. Ball, Multilayered films made from tannic acid and alkaline phosphatasewith enzymatic activity and electrochemical behavior, J. Colloid Interface Sci. 512 (2018) 722–729.

[108] P. Li, K. Chen, L. Zhao, H. Zhang, H. Sun, X. Yang, N.H. Kim, J.H. Lee, Q.J. Niu, Preparation of modified graphene oxide/polyethyleneimine film with enhanced hydrogen barrier properties by reactive layer-by-layer self-assembly, Compos. B Eng. 166 (2019) 663–672.

[109] S.A. Haddadi, A., Ramazani, S.A.,, M., Mahdavian,, M., Arjmand,, Epoxy nanocomposite coatings with enhanced dual active/barrier behavior containing graphene-based carbon hollow spheres as corrosion inhibitor nanoreservoirs, Corros. Sci. 185 (2021), 109428.

[110] A. Vimalanandan, L.P. Lv, T.H. Tran, K. Landfester, D. Crespy, M. Rohwerder, Redox-responsive self-healing for corrosion protection, Adv. Mater. 25 (2013) 6980–6984.

[111] Z. Li, N. Song, Y.-W. Yang, Stimuli-responsive drug-delivery systems based on supramolecular nanovalves, Matter 1 (2019) 345–368.

[112] A. Mathew, S. Parambadath, S.S. Park, C.-S. Ha, Hydrophobically modified spherical MCM-41 as nanovalve system for controlled drug delivery, Microporous Mesoporous Mater. 200 (2014) 124–131.

[113] T. Wang, L. Tan, C. Ding, M. Wang, J. Xu, J. Fu, Redox-triggered controlled release systems-based bi-layered nanocomposite coating with synergistic self-healing property, J. Mater. Chem. A 5 (2017) 1756–1768.

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

[115] H. Cai, P. Wang, D. Zhang, Y. Wang, E. Li, An intelligent self-defensive coating based on sulfide ion responsive nanocontainers for suppression of microbiologically influenced corrosion induced by sulfate reducing bacteria, Corros. Sci. 188 (2021), 109543.

[116] Y. Cao, D. Zheng, X. Li, J. Lin, C. Wang, S. Dong, C. Lin, Enhanced corrosion resistance of superhydrophobic layered double hydroxide films with long-term stability on Al substrate, ACS Appl. Mater. Interfaces 10 (2018) 15150–15162.

[117] M.J. Anjum, J. Zhao, V. Zahedi Asl, G. Yasin, W. Wang, S. Wei, Z. Zhao, W. Qamar Khan, In-situ intercalation of 8-hydroxyquinoline in Mg-Al LDH coating to improve the corrosion resistance of AZ31, Corros. Sci. 157 (2019) 1–10.

[118] Y. Song, Y. Tang, L. Fang, F. Wu, X. Zeng, J. Hu, S.F. Zhang, B. Jiang, H. Luo, Enhancement of corrosion resistance of AZ31 Mg alloys by one-step in situ synthesis of ZnAl-LDH films intercalated with organic anions (ASP, La), J. Magnesium Alloys 9 (2021) 658–667.

[119] S.K. Poznyak, J. Tedim, L.M. Rodrigues, A.N. Salak, M.L. Zheludkevich, L.F. Dick, M.G. Ferreira, Novel inorganic host layered double hydroxides intercalated with guest organic inhibitors for anticorrosion applications, ACS Appl. Mater. Interfaces 1 (2009) 2353–2362.

[120] Y. Mei, J. Xu, L. Jiang, Q. Tan, Enhancing corrosion resistance of epoxy coating on steel reinforcement by aminobenzoate intercalated layered double hydroxides, Prog. Org. Coat. 134 (2019) 288–296.

[121] L.X. Li, Z.H. Xie, C. Fernandez, L. Wu, D. Cheng, X.H. Jiang, C.J. Zhong, Development of a thiophene derivative modified LDH coating for Mg alloy corrosion protection, Electrochim. Acta 330 (2020), 135186.

[122] M. Huang, G. Lu, J. Pu, Y. Qiang, Superhydrophobic and smart MgAl-LDH anti-corrosion coating on AZ31 Mg surface, J. Ind. Eng. Chem. 103 (2021) 154–164.

[123] T. Wen, R. Yan, N. Wang, Y. Li, T. Chen, H. Ma, PPA-containing layered double hydroxide (LDH) films for corrosion protection of a magnesium alloy, Surf. Coat. Technol. 383 (2020), 125255.

[124] E. Alibakhshi, E. Ghasemi, M. Mahdavian, B. Ramezanzadeh, y., Mana,, The effect of interlayer spacing on the inhibitor release capability of layered double hydroxide based nanocontainers, J. Cleaner Prod. 251 (2020), 119676.

[125] A.C. Bouali, N.M. André, M.R. Silva Campos, M. Serdechnova, J.F. dos Santos, S. T. Amancio-Filho, M.L. Zheludkevich, Influence of LDH conversion coatings on the adhesion and corrosion protection of friction spot-joined AA2024-T3/CF-PPS, J. Mater. Sci. Technol. 67 (2021) 197–210.

[126] K.A. Yasakau, A. Kuznetsova, S. Kallip, M. Starykevich, J. Tedim, M.G.S. Ferreira, M.L. Zheludkevich, A novel bilayer system comprising LDH conversion layer and sol-gel coating for active corrosion protection of AA2024, Corros. Sci. 143 (2018) 299–313.

[127] K. Cao, Z. Yu, L. Zhu, D. Yin, L. Chen, Y. Jiang, J. Wang, Fabrication of superhydrophobic layered double hydroxide composites to enhance the corrosion-resistant performances of epoxy coatings on Mg alloy, Surf. Coat. Technol. 407 (2021), 126763.

[128] J. Tedim, M.L. Zheludkevich, A.N. Salak, A. Lisenkov, M.G.S. Ferreira, Nanostructured LDH-container layer with active protection functionality, J. Mater. Chem. 21 (2011) 15464.

[129] L. Wang, Q. Zong, W. Sun, Z. Yang, G. Liu, Chemical modification of hydrotalcite coating for enhanced corrosion resistance, Corros. Sci. 93 (2015) 256–266.

[130] X. He, C. Chiu, M.J. Esmacher, H. Liang, Nanostructured photocatalytic coatings for corrosion protection and surface repair, Surf. Coat. Technol. 237 (2013) 320–327.

[131] P. Xiao, J. Zhang, J. Zhao, M.H. Stenzel, Light-induced release of molecules from polymers, Prog. Polym. Sci. 74 (2017) 1–33.

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

[133] E.V. Skorb, A.G. Skirtach, D,, V., Svirdov,, D.G., Shchukin,, H., Möhwald,, Laser-controllable coatings for corrosion protection, ACS Nano 3 (2009) 1753–1760.

[134] E.V. Skorb, D.V. Sviridov, H. Möhwald, D.G. Shchukin, Light responsive protective coatings, Chem. Commun. (2009) 6041–6043.

[135] C. Cai, Y. Zhang, X. Zou, R. Zhang, X. Wang, Q. Wu, P. Sun, Rapid self-healing and recycling of multiple-responsive mechanically enhanced epoxy resin/graphene nanocomposites, RSC Adv. 7 (2017) 46336–46343.

[136] X. Yin, Y. Zhang, P. Lin, Y. Liu, Z. Wang, B. Yu, F. Zhou, Q. Xue, Highly efficient thermogenesis from Fe_3O_4 nanoparticles for thermoplastic material repair both in air and underwater, J. Mater. Chem. A 5 (2017) 1221–1232.

[137] Y. Zou, L. Fang, T. Chen, M. Sun, C. Lu, Z. Xu, Near-infrared light and solar light activated self-healing epoxy coating having enhanced properties using MXene flakes as multifunctional fillers, Polymers 10 (2018).

[138] L. Fang, J. Chen, Y. Zou, S. Chen, T. Fang, C. Lu, Z. Xu, Self-healing epoxy coatings via focused sunlight based on photothermal effect, Macromol. Mater. Eng. 302 (2017) 1700059.

[139] L. Huang, J. Li, W. Yuan, X. Liu, Z. Li, Y. Zheng, Y. Liang, S. Zhu, Z. Cui, X. Yang, K.W.K. Yeung, S. Wu, Near-infrared light controlled fast self-healing protective coating on magnesium alloy, Corros. Sci. 163 (2020), 108257.

[140] D. Habault, H. Zhang, Y. Zhao, Light-triggered self-healing and shape-memory polymers, Chem. Soc. Rev. 42 (2013) 7244–7256.

[141] A. Lendlein, S. Kelch, Shape-Memory Polymers, in: Kirk-Othmer Encyclopedia of Chemical Technology, 2002.

[142] M.D. Hager, S. Bode, C. Weber, U.S. Schubert, Shape memory polymers: Past, present and future developments, Prog. Polym. Sci. 49–50 (2015) 3–33.

[143] H. Wang, J. Xu, X. Du, Z. Du, X. Cheng, H. Wang, A self-healing polyurethane-based composite coating with high strength and anti-corrosion properties for metal protection, Compos. B Eng. 225 (2021), 109273.

[144] W. Fan, Y. Zhang, W. Li, W. Wang, X. Zhao, L. Song, Multi-level self-healing ability of shape memory polyurethane coating with microcapsules by induction heating, Chem. Eng. J. 368 (2019) 1033–1044.

[145] P.M. Paraskar, M.S. Prabhudesai, R.D. Kulkarni, Synthesis and characterizations of air-cured polyurethane coatings from vegetable oils and itaconic acid, React. Funct. Polym. 156 (2020), 104734.

[146] C. Yu, M. Salzano de Luna, A. Marotta, C. Ponti, I. Esposito, F. Scherillo, Z. Wang, X. Zhang, H. Xia, M. Lavorgna, NIR light-triggered self-healing waterborne polyurethane coatings with polydopamine-coated reduced graphene oxide nanoparticles, Prog. Org. Coat. 161 (2021), 106499.

[147] S.K. Andreas Lendlein, Shape-Memory Polymers, angew Chemie International Edition, 41 (2002) 2034-2057.

[148] G. Li, D. Nettles, Thermomechanical characterization of a shape memory polymer based self-repairing syntactic foam, Polymer 51 (2010) 755–762.

[149] Q. Zhao, H.J. Qi, T. Xie, Recent progress in shape memory polymer: New behavior, enabling materials, and mechanistic understanding, Prog. Polym. Sci. 49–50 (2015) 79–120.

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

[151] Y. Huang, L. Deng, P. Ju, L. Huang, H. Qian, D. Zhang, X. Li, H.A. Terryn, J.M. C. Mol, Triple-action self-healing protective coatings based on shape memory polymers containing dual-function microspheres, ACS Appl. Mater. Interfaces 10 (2018) 23369–23379.

[152] X. Luo, P.T. Mather, Shape memory assisted self-healing coating, ACS Macro Lett. 2 (2013) 152–156.

[153] E., kianfar,, Magnetic nanoparticles in targeted drug delivery: a review, J. Supercond. Novel Magn. 34 (2021) 1709–1735.

[154] W. Wang, W. Li, W. Fan, X. Zhang, L. Song, C. Xiong, X. Gao, X. Liu, Accelerated self-healing performance of magnetic gradient coating, Chem. Eng. J. 332 (2018) 658–670.

[155] J.C. Murphy, R.F. Cohn, Magnetic field measurement of corrosion processes, J. Electrochem. Soc. 135 (1988) 310–313.

[156] J.S.P. Gonzalo, E. Gallo, P.L. Chapman, Corrosion monitoring of metals, Eur. J. Environ. Civil Eng. 15 (2011) 633–647.

[157] L. Wu, A. Mendoza-Garcia, Q. Li, S. Sun, Organic phase syntheses of magnetic nanoparticles and their applications, Chem. Rev. 116 (2016) 10473–10512.

[158] F.N. Sayed, V. Polshettiwar, Facile and sustainable synthesis of shaped iron oxide nanoparticles: effect of iron precursor salts on the shapes of iron oxides, Sci. Rep. 5 (2015) 9733.

[159] T. Hyeon, Chemical synthesis of magnetic nanoparticles, Chem. Commun. (2003) 927–934.

[160] S. van Berkum, J.T. Dee, A.P. Philipse, B.H. Erne, Frequency-dependent magnetic susceptibility of magnetite and cobalt ferrite nanoparticles embedded in PAA hydrogel, Int. J. Mol. Sci. 14 (2013) 10162–10177.

[161] L. Dai, T. Wang, C. Deng, Q. Feng, D. Wang, New method to identify field joint coating failures based on MFL in-line inspection signals, Coatings 8 (2018) 86.

[162] G.L. Li, H. Möhwald, D.G. Shchukin, Silica/polymer double-walled hybrid nanotubes: synthesis and application as stimuli-responsive nanocontainers in self-healing coatings, ACS Nano 7 (2013) 2470–2478.

[163] M. Saremi, M. Yeganeh, Application of mesoporous silica nanocontainers as smart host of corrosion inhibitor in polypyrrole coatings, Corros. Sci. 86 (2014) 159–170.

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

[165] J. Peng, Y. Liu, M. Zhang, F. Liu, L. Ma, C.Y. Yu, H. Wei, One-pot fabrication of dual-redox sensitive, stabilized supramolecular nanocontainers for potential programmable drug release using a multifunctional cyclodextrin unit, J. Controll. Release 334 (2021) 290–302.

[166] G. Granata, S. Stracquadanio, M. Leonardi, E. Napoli, G.M.L. Consoli, V. Cafiso, S. Stefani, C. Geraci, Essential oils encapsulated in polymer-based nanocapsules as potential candidates for application in food preservation, Food Chem. 269 (2018) 286–292.

[167] L. Cheng, L. Kong, X. Zhang, X. Kong, Form-stable phase change nanocapsules with photo and electric dual responses for multipurpose applications in energy storage and conversion, Sol. Energy Mater. Sol. Cells 235 (2022), 111461.

[168] T. Haynes, O. Bougnouch, V. Dubois, S. Hermans, Preparation of mesoporous silica nanocapsules with a high specific surface area by hard and soft dual templating approach: Application to biomass valorization catalysis, Microporous Mesoporous Mater. 306 (2020), 110400.

[169] L. Ma, C. Ren, J. Wang, T. Liu, H. Yang, Y. Wang, Y. Huang, D. Zhang, Self-reporting coatings for autonomous detection of coating damage and metal corrosion: A review, Chem. Eng. J. 421 (2021), 127854.

[170] E.T. van den Dungen, B. Loos, B. Klumperman, Use of a profluorophore for visualization of the rupture of capsules in self-healing coatings, Macromol. Rapid Commun. 31 (2010) 625–628.

[171] J.P. Wang, J.K. Wang, Q. Zhou, Z. Li, Y. Han, Y. Song, S. Yang, X. Song, T. Qi, H. Möhwald, D. Shchukin, G.L. Li, Adaptive polymeric coatings with self-reporting and self-healing dual functions from porous core-shell nanostructures, Macromol. Mater. Eng. 303 (2018) 1700616.

[172] S. Roshan, A.A. Sarabi Dariani, J. Mokhtari, Monitoring underlying epoxy-coated St-37 corrosion via 8-hydroxyquinoline as a fluorescent indicator, Appl. Surf. Sci. 440 (2018) 880–888.

[173] X. Yuan, S. Dong, Q. Zheng, W. Yang, T. Huang, Novel and efficient curcumin based fluorescent polymer for scale and corrosion inhibition, Chem. Eng. J. 389 (2020), 124296.

[174] P.P. Anna, A. Panova, D.R. Walt, In situ fluorescene imaging of localized corrosion with a pH-sensitive imaging fiber, Anal. Chem. 69 (1997) 1635–1641.

[175] X. Liu, H. Spikes, J.S.S. Wong, In situ pH responsive fluorescent probing of localized iron corrosion, Corros. Sci. 87 (2014) 118–126.

[176] A. Augustyniak, W. Ming, Early detection of aluminum corrosion via "turn-on" fluorescence in smart coatings, Prog. Org. Coat. 71 (2011) 406–412.

[177] A. Augustyniak, J. Tsavalas, W. Ming, Early detection of steel corrosion via "turn-on" fluorescence in smart epoxy coatings, ACS Appl. Mater. Interfaces 1 (2009) 2618–2623.

[178] D.E. Bryant, D. Greenfield, The use of fluorescent probes for the detection of under-film corrosion, Prog. Org. Coat. 57 (2006) 416–420.

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

[180] F. Maia, J. Tedim, A.C. Bastos, M.G. Ferreira, M.L. Zheludkevich, Nanocontainer-based corrosion sensing coating, Nanotechnology 24 (2013), 415502.

[181] T.L.P. Galvão, I. Sousa, M. Wilhelm, J. Carneiro, J. Opršal, H. Kukačková, V. Špaček, F. Maia, J.R.B. Gomes, J. Tedim, M.G.S. Ferreira, Improving the functionality and performance of AA2024 corrosion sensing coatings with nanocontainers, Chem. Eng. J. 341 (2018) 526–538.

[182] D. Mata, N. Scharnagl, S.V. Lamaka, E. Malheiro, F. Maia, M.L. Zheludkevich, Validating the early corrosion sensing functionality in poly (ether imide) coatings for enhanced protection of magnesium alloy AZ31, Corros. Sci. 140 (2018) 307–320.

[183] S. Chen, Y. Hong, Y. Liu, J. Liu, C.W. Leung, M. Li, R.T. Kwok, E. Zhao, J.W. Lam, Y. Yu, B.Z. Tang, Full-range intracellular pH sensing by an aggregation-induced emission-active two-channel ratiometric fluorogen, J. Am. Chem. Soc. 135 (2013) 4926–4929.

[184] J. Mei, N.L. Leung, R.T. Kwok, J.W. Lam, B.Z. Tang, Aggregation-induced emission: together we shine, united we soar!, Chem. Rev. 115 (2015) 11718–11940.

[185] M.J. Robb, W. Li, R.C. Gergely, C.C. Matthews, S.R. White, N.R. Sottos, J. S. Moore, A robust damage-reporting strategy for polymeric materials enabled by aggregation-induced emission, ACS Cent. Sci. 2 (2016) 598–603.

[186] T.H. Lee, Y.K. Song, S.H. Park, Y.I. Park, S.M. Noh, J.C. Kim, Dual stimuli responsive self-reporting material for chemical reservoir coating, Appl. Surf. Sci. 434 (2018) 1327–1335.

[187] L. Ruggiero, L. Crociani, E. Zendri, N. El Habra, P. Guerriero, Incorporation of the zosteric sodium salt in silica nanocapsules: synthesis and characterization of new fillers for antifouling coatings, Appl. Surf. Sci. 439 (2018) 705–711.

[188] B. Qian, Z. Zheng, C. Liu, M. Li, R.A. D'Sa, H. Li, M. Graham, M. Michailidis, P. Kantserev, V. Vinokurov, D. Shchukin, Microcapsules prepared via pickering emulsion polymerization for multifunctional coatings, Prog. Org. Coat. 147 (2020), 105785.

[189] H. Yang, X. Guo, R. Chen, Q. Liu, J. Liu, J. Yu, C. Lin, J. Wang, M. Zhang, Enhanced anti-biofouling ability of polyurethane anti-cavitation coating with ZIF-8: A comparative study of various sizes of ZIF-8 on coating, Eur. Polym. J. 144 (2021), 110212.

[190] X. Hao, D. Qin, W. Wang, W. Li, H. Feng, Q. Wang, S. Chen, Potential non-releasing bacteria-triggered structure reversible nanomicelles with antibacterial properties, Chem. Eng. J. 403 (2021), 126334.

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

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

[193] Q.B. Guo, K.T. Lau, M.Z. Rong, M.Q. Zhang, Optimization of tribological and mechanical properties of epoxy through hybrid filling, Wear 269 (2010) 13–20.

[194] H. Li, Y. Cui, H. Wang, Y. Zhu, B. Wang, Preparation and application of polysulfone microcapsules containing tung oil in self-healing and self-lubricating epoxy coating, Colloids Surf., A 518 (2017) 181–187.

[195] H.S.X. Zhu, Exciton characteristics in graphene epoxide, ACS Nano 8 (2014) 1284–1289.

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

[197] H. Gong, C. Yu, L. Zhang, G. Xie, D. Guo, J. Luo, Intelligent lubricating materials: A review, Compos. B Eng. 202 (2020), 108450.

[198] N.W. Khun, D.W. Sun, M.X. Huang, J.L. Yang, C.Y. Yue, Wear resistant epoxy composites with diisocyanate-based self-healing functionality, Wear 313 (2014) 19–28.

[199] H. Li, Y. Cui, Z. Li, Y. Zhu, H. Wang, Fabrication of microcapsules containing dual-functional tung oil and properties suitable for self-healing and self-lubricating coatings, Prog. Org. Coat. 115 (2018) 164–171.

[200] K. Li, Z. Liu, C. Wang, W. Fan, F. Liu, H. Li, Y. Zhu, H. Wang, Preparation of smart coatings with self-healing and anti-wear properties by embedding PU-fly ash absorbing linseed oil microcapsules, Prog. Org. Coat. 145 (2020), 105668.

[201] Y. Ren, G. Liu, H. Yang, T. Tong, S. Xu, L. Zhang, J. Luo, C. Zhang, G. Xie, Dynamic wear sensor array based on single-electrode triboelectric nanogenerators, Nano Energy 68 (2020), 104303.

[202] O. Rifaie-Graham, E.A. Apebende, L.K. Bast, N. Bruns, Self-reporting fiber-reinforced composites that mimic the ability of biological materials to sense and report damage, Adv. Mater. 30 (2018) 1705483.