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Historical Perspective

Developments in anticorrosive organic coatings modulated by nano/microcontainers with porous matrices

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ABSTRACT

The durability and functionality of many metallic structures are seriously threatened by corrosion, which makes the development of anticorrosive coatings imperative. This state-of-the-art survey explores the recent developments in the field of anticorrosive organic coatings modulated by innovations involving nano/microcontainers with porous matrices. The integration of these cutting-edge delivery systems seeks to improve the protective properties of coatings by enabling controlled release, extended durability, targeted application of corrosion inhibitors, and can be *co*-constructed to achieve defect filling by polymeric materials. The major highlight of this review is an in-depth analysis of the functionalities provided by porous nano/microcontainers in the active protection and self-healing of anticorrosive coatings, including their performance evaluation. In one case, after 20 days of immersion in 0.1 M NaCl, a scratched coating containing mesoporous silica nanoparticles loaded with an inhibitor benzotriazole and shelled with polydopamine (MSNs-BTA@PDA) exhibited coating restoration indicated by a sustained corrosion resistance rise over an extended period monitored by impedance values at 0.01 Hz frequency, rising from 8.3×10^4 to 7.0×10^5 Ω cm^2, a trend assigned to active protection by the release of inhibitors and self-healing capabilities. Additionally, some functions related to anti-fouling and heat preservation by nano/microcontainers are highlighted. Based on the literature survey, some desirable properties, current challenges, and prospects of anticorrosive coatings doped with nano/microcontainers have been summarized. The knowledge gained from this survey will shape future research directions and applications in a variety of industrial areas, in addition to advancing smart corrosion prevention technology.

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1. Introduction

Anticorrosive coatings are specific protective layers that are applied to surfaces, primarily metals, to stop or lessen the harmful effects of corrosion. Materials can become weaker, have a shorter lifespan, and lose usefulness due to corrosion, a natural process triggered by environmental variables and chemical reactions. Anticorrosive coatings serve as a protective barrier between the substrate and its corrosive environment, protecting it from exposure to moisture, chemicals, and other corrosive substances. Even in severe environments, these coatings are made to adhere to the substrate firmly and offer durable protection [1,2]. Numerous industries, including automobile, aerospace, marine, infrastructure, and electronics, use anticorrosive coatings. These coatings, whether applied to machinery, pipelines, bridges, or automobiles, are essential for preventing material deterioration, lowering maintenance costs, and preserving the dependability and integrity of vital structures and parts. The field of anticorrosive coatings is constantly innovating, providing fresh approaches to overcome the problems caused by corrosion and increase the lifespan of diverse materials.

Innovative developments in coating technology have been sparked by the search for improved coatings with multifunctional features. The ongoing research into mitigation strategies against corrosion, one of the many difficulties encountered by industry, calls for creative solutions to safeguard important assets and infrastructure. While still somewhat effective, conventional protective coatings frequently lack the adaptability needed to handle the complexity of contemporary surroundings. In response, scientists have developed innovative techniques that combine the benefits of organic and inorganic materials, creating a new paradigm for corrosion protection and other fields [3–5].

A prominent example of this innovative technique lies in the integration of porous nano/microcontainers within organic coatings [6–8]. Among the materials in the class of porous nano/microcontainers applied in organic coatings are mesoporous silica, metal organic frameworks, porous carbon, nano-clay, zeolite, apatite, and calcium carbonate. The intriguing combination of these materials in organic coating harnesses the advantages of both worlds: the tailored functionality and versatility of organic polymers, and the structural precision and controlled release capabilities of porous materials. The outcome is a new class of coatings that not only provides a robust barrier against corrosion but also exhibits a spectrum of additional functionalities, including response to environment changes, effectively ushering in a new era of smart coatings.

The essence of this integration lies in the remarkable properties of porous nano/microcontainers. These nanostructures possess a defined hierarchical porosity, allowing for the encapsulation and controlled release of various active agents [9–11]. When synergistically incorporated within organic coatings, these containers serve as reservoirs for corrosion inhibitors, self-healing agents, and more [12–15]. This reservoir-based approach not only prolongs the effectiveness of the coatings but also offers the capability to tailor the release rates of these agents based on environmental triggers, enabling adaptive responses to varying conditions This principle allows the fabrication of the so-called "smart" coating.

The idea of smart coatings has developed from producing coatings with specific purposes to coatings with inert components that give special properties to coatings with the capacity to sense and react consistently and predictably to environmental changes. One type of smart coating that is fascinating is self-healing coating. It has the dual role of preventing corrosion of the metal substrate and healing itself from damage so that the coating can return to its original state to a reasonable extent with little or no external intervention. The term "self-healing" coatings refers to the capacity of these coatings to regain their original qualities, which sets them apart from traditional non-healing coatings that serve primarily to protect metal substrates from corrosive conditions. The phrase "self-healing coatings" is sometimes primarily used to describe coatings that can seal a defect in the coating, whereas the term "active anticorrosion coatings" refers to coatings that have active ingredients (such as corrosion inhibitors) preloaded into them that work to autonomously prevent corrosion on the metal surface. Both classes of coatings are regarded by some researchers as "self-healing" coatings and they can be combined to fabricate coatings with many protective mechanisms through multifunctional pathways, with nano/microcontainers playing a major role [16–18].

In this state-of-the-art survey, the synthesis and characterization of porous nano/microcontainers, their incorporation into organic coatings, the mechanisms of corrosion protection and functional release, as well as the intriguing applications and prospects of these multifunctional coatings, is covered in more detail in the sections. The review begins with a general overview of the difficulties associated with conventional anticorrosive coatings, a brief concept of porous nano/microcontainers, and emphasizes the importance of these nano/microcontainers in overcoming the constraints of conventional anticorrosive coating. Through this survey, we seek to shed light on the revolutionary potential of fusing nano/microcontainers in organic matrices, ultimately moving corrosion protection and functional coatings into a new era of robust performance and adaptability. This review attempts to give academics, engineers, and industry experts a comprehensive grasp of the implications of nano/microcontainers bearing porous matrices in the performance of coatings by an extensive survey of the literature.

2. A brief concept of porous nano/microcontainers

Anti-corrosive coatings play a crucial role in protecting metallic substrates from degradation caused by environmental factors. In recent years, porous nano/microcontainers have emerged as promising tools to improve the efficiency and longevity of anti-corrosive coatings. These containers are designed to encapsulate and release active corrosion inhibitors in a controlled manner, mitigating the progression of corrosion damage. This section delves into the various types of porous containers used in anti-corrosive coatings, their properties, synthesis and fabrication techniques of porous nano/microcontainers, and the characterization techniques to evaluate container properties.

2.1. Types of porous nano/microcontainers

Porous nano/micro-containers come in various forms, each offering distinct advantages for corrosion protection. Notable types include but are not limited to mesoporous silica nanoparticles (MSNs), halloysite nanotubes (HNT), layered double hydroxide (LDH) nanocapsule, metal-organic framework (MOF), zeolite and other polymeric nano/microcapsules. Nano/microcapsules are widely studied for their ability to encapsulate corrosion inhibitors [19]. As the name implies, these containers are typically composed of biocompatible polymers (liquid/solid core coated with a polymeric shell) and can be loaded with various inhibitor types. The solid/oil core of nanocapsules, for example, significantly improves the inhibitor loading capacity while lowering the polymeric matrix content of nanoparticles. Their porous structure allows controlled inhibitor release, providing sustained protection over time [20]. Mesoporous silica nanoparticles (MSNs) are inorganic-based solid nanomaterials made of a colloidal amorphous silicon dioxide matrix that has thousands of ordered pores arrayed in a three-dimensional (3D) network structure within the mesoporous range [21]. MSNs possess well-defined pore structures that can accommodate corrosion inhibitors [22]. Their high surface area and tuneable pore sizes make them suitable candidates for encapsulation and controlled release [23]. MSNs have several advantages, such as a chemically stable structure, low reactivity, and compatibility with numerous matrices [24]. They are easily synthesized [25], and their high surface area and mesoporous structure are very attractive for adsorption and desorption-related applications [22]. Layered double hydroxides (LDHs) are lamellar compounds with exchangeable anions in the interlayer region. They store corrosion inhibitors through electrostatic adsorption [26]. LDH nanosheets offer an advantageous platform for inhibitor encapsulation due to their intercalation capabilities [27]. Inhibitors can be intercalated between the layers, and the LDH structure provides protection against inhibitor leaching [27,28]. The crystalline micro/mesoporous hybrid materials known as metal-organic frameworks (MOFs) are made of metal ions or clusters joined by organic linkers. MOFs exhibit a unique porous structure with the potential for hosting inhibitors within their frameworks [29]. The crystalline nature of MOFs allows for precise control over pore size and functionality, enabling tailored inhibitor release kinetics [4]. Halloysite nanotubes (HNTs) are inorganic materials chemically the same as kaolinite. They are multi-layered structures comprising tetrahedral SiO_4 and octahedral AlO_6 layers arranged in a 1:1 ratio [30]. HNTs are suitable candidates for smart coating due to their natural properties, low cost, availability, ease of encapsulation and negatively charged polarity that can easily be modified [31–33]. HNTs come in various forms, but the tubular morphology is the most dominant [31]. Corrosion inhibitors can be loaded into HNTs by soaking them in an inhibitor solution or by agitating the suspension of capsules and fillers [34]. Zeolites are crystalline aluminosilicates with well-defined pore structures. They can accommodate corrosion inhibitors and ion-exchange compounds, providing controlled release mechanisms and their influence on the performance of anti-corrosive coatings. According to Jomy et al. [35], most nano/microcontainers are preloaded with various forms of corrosion inhibitors and are usually made in containers or reservoirs such as $CaCO_3$ microbeads, TiO_2 nanocontainers, carbon nanosheets, polyelectrolyte nanocapsules, chitosan microspheres, silica/Lacithin, CeO_2 hollow spheres and Eudragit polymeric particles, among others. Typically, when there is ingress of corrosive species, these containers release inhibitors or healing agents on demand to passivate defect regions in the coating as illustrated in Fig. 1.

2.2. Properties of nano/microcontainers

2.2.1. Structural characteristics

The structural characteristics of nano/micro-containers influence their loading capacity, controlled release, delivery, stability, size and surface area, and durability. Porous nano/micro-containers exhibit distinct structural features based on their composition and synthesis methods [36]. Studies show that high porosity and surface area facilitate the loading of a significant amount of inhibitor, enhancing the protective capabilities of coatings [37]. In addition, porous containers enable the controlled release of inhibitors, maintaining a steady concentration at the metal-coating interface and extending the coating's efficacy. MSNs are spherical and stable. They possess high surface area and well-defined pore structures with excellent loading and release capabilities, making them suitable containers for corrosion inhibition applications. HNTs have a variety of morphologies with structures that allow for easy encapsulation and loading of inhibitors, the most common of which is tubular. MOFs made of metal ions and organic ligands have high surface areas and tuneable porosities, enabling inhibitor encapsulation. LDHs are layered and suited for intercalating anionic inhibitors. Zeolites, with their crystalline aluminosilicate framework, offer uniform pore sizes for controlled diffusion of active agents.

2.2.2. Loading capacities

One of the critical aspects of porous nano/microcontainers is their loading capacity for corrosion inhibitors and other active substances. Mesoporous silica nanoparticles (MSNs), halloysite nanotubes (HNTs), and layered double hydroxides (LDH) are often used as nano-containers in self-healing smart coatings due to their high inhibitor load capacity [38]. Silica containers possess high loading capacities due to their size and functionalization ability. Borisova et al. synthesized silica containers with a large pore volume and surface area, suggesting a high inhibitor loading capacity [37]. On the other hand, HNTs possess internal lumen and interspaces for sufficient loading of inhibitors up to 5 % – 20 % by weight, depending on the size of the outer and inner diameters [31,33].

2.2.3. Release kinetics

The controlled release of active agents from the containers significantly influences the efficacy of anti-corrosive coatings. The inhibitor release rate ensures fast delivery of effective protective dosages, limits excessive and unwanted release, achieves long-term release, and responds to local environmental changes [31]. MOFs exhibit tuneable release kinetics based on their porosity and structure, silica nanoparticles release inhibitors through diffusion, LDHs release inhibitors gradually as the layers break down, offering sustained protection, and Zeolites facilitate controlled ion exchange, resulting in predictable release rates. Several factors influence the release kinetics of nano/micro containers, e.g. pH, UV light, temperature, concentration, etc. [39,40]. Li et al. [31] examined the stimuli-responsive release capabilities of microcapsules (MCs) for 2-mercaptobenzothiazole (2-MBT) and concluded that 2-MBT solubility and polyelectrolyte film porosity controlled the release of 2-MBT from MCs. Mekeridis et al. [41] also investigated the release kinetics of inhibitors from nano-containers in the presence of aluminum alloys 2024-T3 (AA2024-T3) and found that the protectiveness of the metal alloy depended on the concentration of the nano-container.

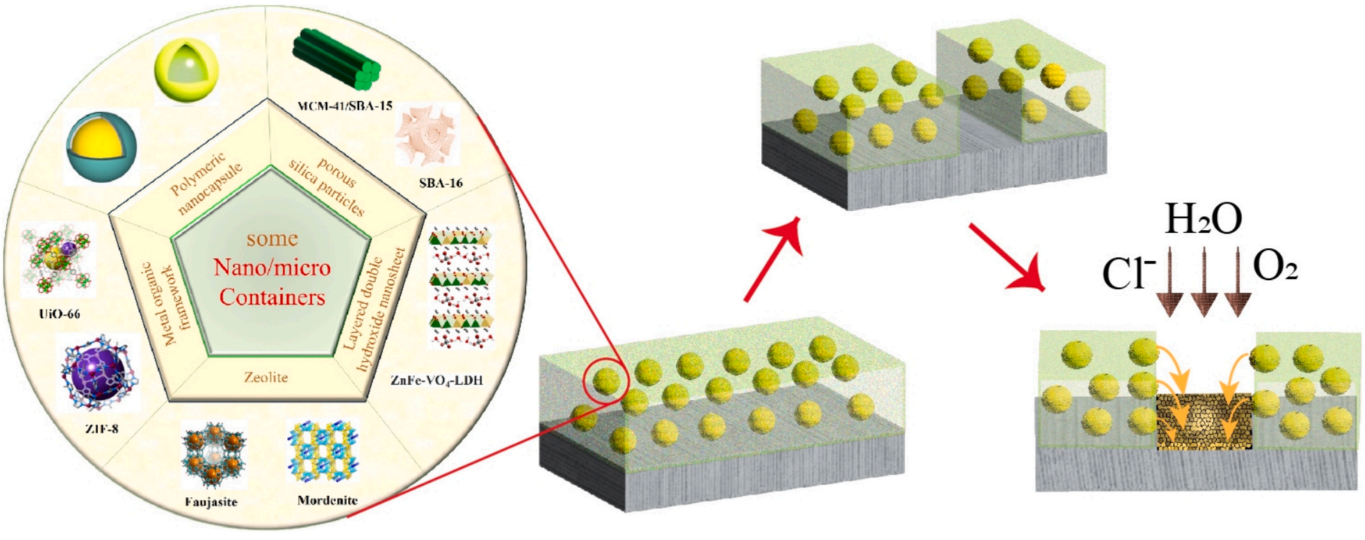

Fig. 1. Illustration of the release of inhibitors by nano/microcontainers to passivate the substrate in a defect region.

2.2.4. *Barrier functionality*

Porous nano/microcontainers contribute to the barrier properties of anticorrosive coatings [42]. When uniformly distributed within the coating matrix, the containers hinder the diffusion of corrosive species, extending the coating's protective effect. This property is particularly advantageous in aggressive environments where barrier performance is crucial. Hayatdavoudi and Rahsepar in their study attributed the protection performance of the zinc-rich epoxy coating to the barrier effect of the MBT-intercalated LDH nanocontainers. They further stated that the 2D-planar morphology of LDH particles had a partially blocking effect on the small pores of the coating layer, providing a barrier against diffusion of aggressive species which in turn result in improvement of coating resistance [43].

2.2.5. *Self-healing potential*

The self-healing potential of nano/micro-containers is one of the intrinsic properties required to enhance the longevity of coatings. Nanocontainers such as poly(urea-formaldehyde) microcapsules (PUF), poly(melamine formaldehyde) microcapsules (PMF), cellulose nanofibers (CNF), and halloysite nanotube (HNT) loaded with corrosion inhibitors are a few examples [20]. These containers are designed to trap inhibitors within the core of their shell and release the active agents in response to localized damage, promoting autonomous repair mechanisms. The self-healing properties of nano and micro containers are influenced by several factors such as temperature, core-shell thickness, release rates, etc. Numerous studies have been performed on the self-healing performance of coatings [20,31,44]. This capability significantly advances corrosion protection technology, reducing maintenance requirements and increasing the lifespan of coatings. Li et al. designed smart microcapsules with excellent self-healing ability and long-term life span [31]. The smart container served in a dual capacity, ensuring the fast release of the active substance and curtailing waste. The self-healing mechanism is schematically depicted in Fig. 2 a-d. The existence of released 2-MBT to control corrosion in the defected region of the coating is evidenced by their characteristic peaks appearing in the FTIR spectra as shown in Fig. 2 e. Moreover, the suppression of corrosion for the hybrid coating was confirmed using AFM, as shown in Fig. 2 f and g.

2.3. *Synthesis and fabrication techniques of porous containers*

Tailored synthesis and fabrication methods are pivotal for designing efficient anticorrosive coatings. The properties of porous nano/microcontainers can be adjusted to achieve controlled release, optimized barrier performance, and enhanced self-healing capabilities, contributing to prolonged corrosion protection. There are several methods for synthesizing nano/microcontainers, a combination of two or more methods can also be utilized. Some of the most employed synthesis techniques include the sol-gel method, polymerization method, layer-by-layer method, and template-assisted method. Other synthesis techniques include hydrothermal [43], electrostatic self-assembly, solvothermal [45] and co-precipitation [46] techniques.

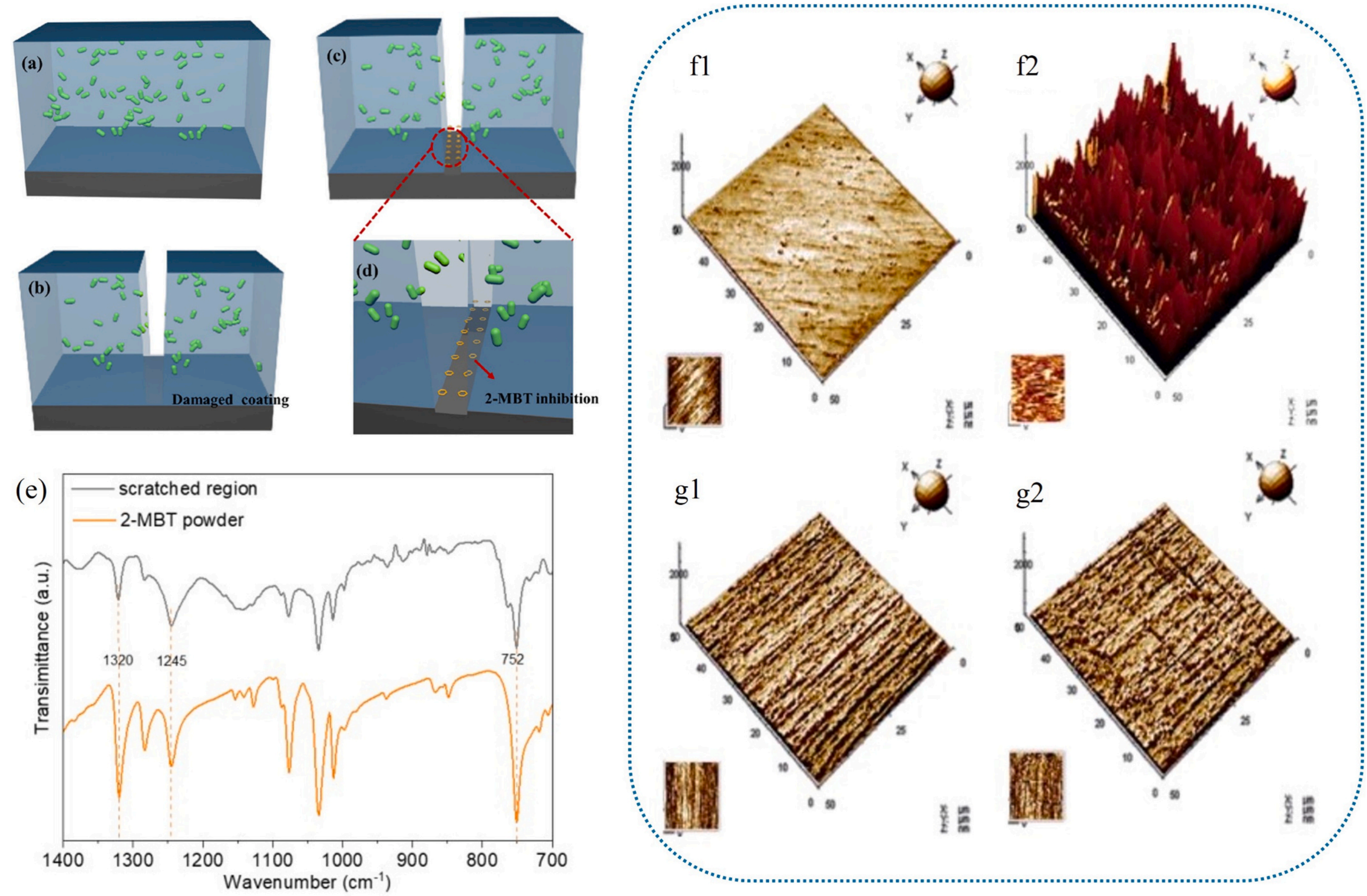

Fig. 2. Schematic of the mechanism of active self-healing of hybrid coatings including (a) a compact coating embedded with MCs, (b) a scratched MC-embedded coating, and (c and d) release of the inhibitor from the MC-embedded coating and adsorption of the inhibitor on the metal surface; (e) FTIR spectra of 2-MBT powder and products obtained from the scratched region of the hybrid coating; and AFM photos of scratched coatings immersed in NaCl solution for (1) 0 h and (2) 6 h with (f) 0 wt% and (g) 5 wt% MCs embedded [31].

2.3.1. *Sol-Gel method*

This is the most common method for preparing metal oxide-based particle systems. It involves the transformation of liquid precursors into sol, followed by gelation to form solid nano/microcontainers (Fig. 3a) [47]. It is cost-effective and allows precise control over container composition, porosity, thickness, and morphology. By modifying parameters like precursor type, solvent, and pH, sol-gel enables the fabrication of containers tailored for specific corrosion protection needs.

2.3.2. *Polymerization method*

Polymerization techniques are used to develop polymeric capsules. This method is easy and allows for controlled microcapsule size and shell thickness [20]. First, the inhibitor is dispersed in distilled water and continuously stirred to form an emulsion. Later, monomers and cross-linkers are added to the emulsion to form polymeric microcapsules over the inhibitor. Fig. 3b and c depicts schematic concepts for the in-situ emulsion polymerization process for producing polymeric containers. Schreiner et al. [48] fabricated microcapsules based on thermoset resins (urea–formaldehyde and melamine–formaldehyde), which was composed of components with several chemical natures (resins or inhibitors) using emulsion polymerization techniques (Fig. 3b). Sun et al. [49] also synthesized a double-layered capsule shell containing liquid 4,40-bis-methylene cyclohexane diisocyanate (HMDI) with excellent stability and superior water resistance using interfacial and in-situ polymerizations in an oil/water emulsion system (Fig. 3c). The polyurea microcapsules with an average diameter of 74.2 ± 14.0 μm were first prepared by interfacial polymerization and then coated with a layer of PUF shell with a thickness of 1.52 ± 0.21 μm using in situ polymerization. Several other studies have also employed this technique in the synthesis of nano/microcontainers.

2.3.3. *Layer-by-layer (LbL) technique*

This multilayer deposition process is intriguing for creating self-healing epoxy coatings. Self-assembly (LBL) method was first introduced by Iler in 1966 in a work on colloidal particles [50]. Shchukin originally used this technique in self-healing coating. Shchukin et al. [51] in their study described the LbL electrostatic deposition of oppositely charged polyelectrolyte layers on a metal surface with multiple functions. LBL technique has gained popularity in recent times [31,44,52]. Li et al. [31] fabricated smart microcapsules (MCs) using the LBL technique. The authors first deposited positively charged polyelectrolytes ε-poly-L-lysine (ε-PLL) on 2-mercaptobenzothiazole (2-MBT)-loaded halloysite clay nanotubes (HNT) nanoparticles, then the suspension was allowed to remain for 10 mins to allow the ε-PLL layer to encapsulate. Following this, the MCs were separated via centrifugation and cleaned three times with distilled water. The second layer of negatively charged SA was deposited on ε-PLL/(HNTs@2-MBT), and the suspension was allowed to stand for 10 mins to allow the encapsulation of the SA layer. After encapsulation, the fabricated MCs were separated by centrifugation and washed with distilled water, then were dried in an electric oven at 50 °C for 48 h. A schematic diagram of the fabrication process of smart MCs using the LbL technique is presented in Fig. 3d. Sonawane et al. [52] also fabricated a ZnO nano container using the LbL technique where ZnO was used as the core based on its anticorrosive

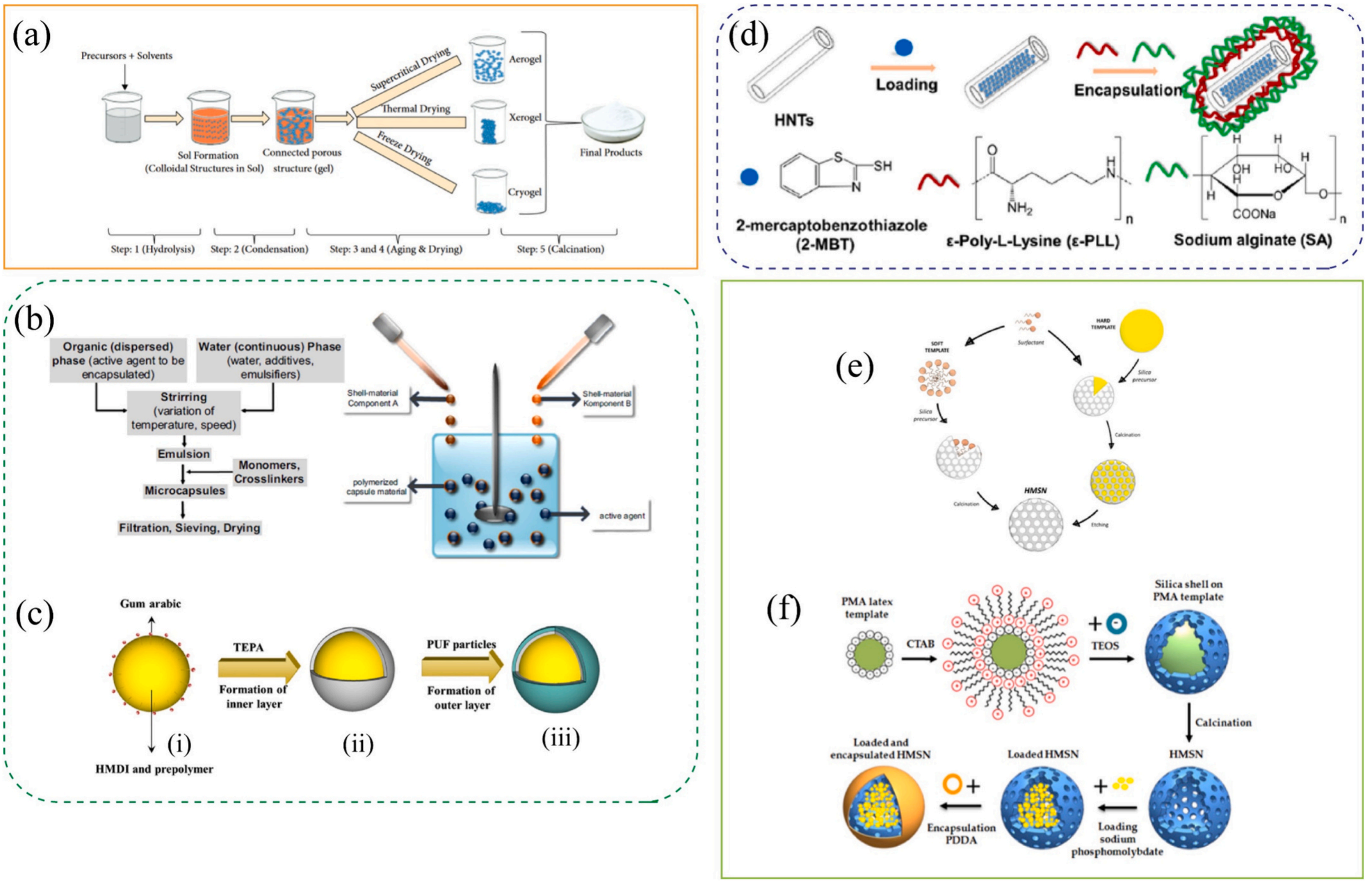

Fig. 3. Schematic of (a) different stages of sol-gel process: from precursor to aerogel [47]; (b) in-situ emulsion polymerization process for making polymeric containers [48]; (c) the formation process of double-layered microcapsule: (i) a single oil droplet after emulsification for 45 min, (ii) the inner layer of one microcapsule was formed along with the introduction of TEPA solution in emulsion system, and (iii) the outer wall of one microcapsule was formed through the deposition of PUF particles [49]; (d) the fabrication process of smart MCs using the LbL technique [31]; (e) hard and soft templating in HMSN synthesis [54]; and (f) Synthesis of HMSN, loading with sodium phosphomolybdate and deposition of an external PDDA layer [56].

properties. Qian et al. [44] employed the LbL technique in the synthesis of a novel nano-container with a final structure composed of SiO_2/chitosan/alginate/polyaspartic acid/alginate/polyaspartic acid. In this case, SiO_2 was used as the core. This method has found wide applicability in enhancing the performance of anticorrosive coatings and is still being studied.

2.3.4. Template-assisted methods

Template-assisted methods utilize sacrificial templates to guide container formation. In the commonly used sacrificial template method, templates are made of polystyrene latex, chitosan-polyacrylic acid, polyvinylpyrrolidone, calcium carbonate nanoparticles, and assemblies of Fe_3O_4 nanocrystals [53]. Hard templates, like colloidal particles, and soft templates, such as micelles, enable control over container size, shape, and porosity (Fig. 3e) [54]. Template method is one of the commonest methods for the synthesis of MSNs [55]. It provides the versatility needed to tailor container properties for specific anticorrosive coating applications. Zea et al. [56] synthesized hollow mesoporous silica nanoparticles (HMSN) using the template method. Sodium phosphomolybdate was loaded into HMSN encapsulated by a simple deposition of one layer of an oppositely charged polyelectrolyte, poly(diallyldimethylammonium chloride) (PDDA) according to Fig. 3f. Guo et al. [57] also synthesized spherical and uniform-sized MSNs with suitable pore structures that allows for easy loading of inhibitors using the template method.

2.4. Characterization techniques to evaluate container properties

Characterization techniques are essential for container evaluation and optimisation. A combination of different techniques such as microscopic, spectroscopic, electrochemical, and others, are often employed to study the properties of containers. Some of the most common techniques are listed in Table 1.

3. Overview of anticorrosive coatings and their applications

Typically, an anticorrosive coating is placed on a metallic surface, to protect it from corroding that might happen spontaneously when exposed to any aggressive environment. Usually, an anticorrosive coating system consists of multiple layers of distinct coatings with different properties and purposes. The various coats may be metallic, inorganic, or organic depending on the desired qualities of the coating system. For maximum and effective corrosion protection, the coatings must be homogeneous, well-adherent, pore-free, and self-healing for situations where physical defects to the coating may occur. Anticorrosion coatings are made up of five major component groups: binder, fillers, additives, pigments, and carrier. They can be fabricated using a wide range of substances, materials, or chemical combinations. Additives are secondary products that are incorporated in minute amounts to enhance coating characteristics or to address technical issues.

The carrier is one of the important components of anticorrosive coatings, even if it does not play a major role in the protective processes offered by the coatings. The carrier, which is only present in uncured condition, is the vehicle that carries all the components in uncured paint. In addition to dissolving or dispersing the components, the carrier can reduce the viscosity of the coating, which facilitates spraying or drenching and makes it easier to apply. The solvent used as the carrier can be gaseous, liquid, or organic, depending on the type of coating. The carrier's main responsibility will be to soak the surface while it is liquid, regulating the coating film's homogeneity.

The binder provides the physical framework for the polymer, enables support, and contains the additives and pigments. It adheres to these components as well as the surface of the metal. It not only gives structure, but it also ensures that the most desirable properties of the coating - cohesion within the coating, adhesion to the metal, robust mechanical resistance, and low permeability—are preserved. It is obvious that

Table 1
Characterization techniques for nano/microcontainers and particles.

Characterization technique	Functionality and application	Samples studied	Ref(s).
Scanning Electron Microscopy (SEM)	Analysis of the morphology of the containers and synthesized particles	Mesoporous silica particles (MSPs)	[23]
		Carbon nanotube (CNT) and covalent organic framework (COF)	[45]
		Halloysite nanotubes and microcapsules	[31,32]
		Polyaspartic acid (PASP) impregnated SiO_2-based nanocontainer	[44]
Transmission Electron Microscopy (TEM)	High-resolution study of the morphology, pore structure, pore size distribution, pore volume and internal structures of nano/microcontainers and particles	Mesoporous silica particles (MSPs)	[23]
		Mesoporous silica nanocontainers (NCs)/spherical hollow silica microcontainers (SHS)	[37]
		Carbon nanotube (CNT) and covalent organic framework (COF)	[45]
		Halloysite nanotube (HNT)	[31,32]
X-ray Diffraction (XRD)	Analysis of the crystalline structure of porous containers, phase analysis	Carbon nanotube (CNT) and covalent organic framework (COF)	[45]
		LDH nanocontainers	[43]
		Hollow mesoporous titanium dioxide nanosphere (HMTNs)	[58]
UV–vis Spectroscopy	Release kinetics studies	Mesoporous silica particles (MSPs)	[23]
		Halloysite nanotube (HNT)	[32]
		Organic inhibitor species from LDH nanocontainers	[43]
		Microcapsules	[31]
		Benzotriazole (BTA) filled in sealed hollow mesoporous titanium dioxide nanosphere (HMTN−BTA@ZnO-QDs)	[58]
Fourier-Transform Infrared Spectroscopy (FTIR)	Identification of functional groups and chemical bonding within the container	Mesoporous silica particles (MSPs)	[23]
		Carbon nanotube (CNT) and covalent organic framework (COF)	[45]
		Polyaspartic acid (PASP) impregnated SiO_2-based nanocontainer	[44]
Thermogravimetric Analysis (TGA)	Investigation of the thermal stability and loading capacities of containers	Carbon nanotube (CNT) and covalent organic framework (COF)	[45]

(continued on next page)

Table 1 (*continued*)

Characterization technique	Functionality and application	Samples studied	Ref(s).
		Mesoporous silica nanocontainers (NCs) and spherical hollow silica microcontainers (SHS)	[37]
		Benzotriazole (BTA) filled in sealed hollow mesoporous titanium dioxide nanosphere (HMTN−BTA@ZnO-QDs)	[58]
		2-mercaptobenzothiazole (2-MBT) in HNT	[31]
Electrochemical Impedance Spectroscopy (EIS)	Evaluation of barrier functionality and self-healing properties of containers in coatings	Investigated the corrosion protection performance and self-healing potential of the nano-containers	[44]
Scanning Vibrating Electrode Technique (SVET)	Analysis of the local self-healing effect of the coatings	Coatings container SiO_2 impregnated with Polyaspartic acid (PASP)	[44]
Confocal Raman spectroscopy	Functional group analysis	Carbon nanotube (CNT) and covalent organic framework (COF)	[45]
ICP-MS	Ion release analysis	Investigated the anti-corrosion potency of the nanoparticle in the solution phase	[45]
Microelectrophoresis/ Zeta Potential Analyzer	Analyzing the surface charge and average effective diameter in colloidal Solutions	HNTs, PLL-encapsulated HNTs, and MCs	[31,32]

selecting the right binder is crucial because the chemical composition and curing of an anticorrosive coating determine its properties. The performance of coating materials is frequently correlated with the benefits and drawbacks of its binder family.

There are three different types of pigments: inhibitive, sacrificial, and barrier pigments [59]. The different types of pigment vary in terms of the coating's thickness and their defense systems as shown in Fig. 5a. When analyzing the anticorrosive capabilities, the binder and pigments are the most crucial components among the five categories. While the binder determines the overall characteristics of anticorrosive coatings, pigments are essential when thinking about the protection mechanisms. The Steel will be shielded initially from the possibly corrosive environment by an anticorrosive coating. It's crucial to quickly review what corrosion is and how it works to comprehend in what ways these coatings can preserve steel. Corrosion is characterized as a physicochemical process in which the environment interacts with a substance to modify its properties (metal consumption/dissolution). It is a procedure that may be influenced by a distinction between the cathode and anode locations. Alternative to being adjacent to one another, the anode and cathode locations might be spaced apart. The less noble or more energetically dense area of the metal surface is where the anode is located. Water, oxygen, or additional reducible species, an anode-to-cathode electrolyte channel, a cathode site, and other factors are all necessary for corrosion to occur. When fabricating an organic coating, the major objective is to restrict one or more of these factors because they can all have an impact on the corrosion rate. As a result, the primary defenses exhibited by organic coating are: establishing a strong barrier against the corrosion-causing water, oxygen, and ions; establishing an electrical route with a very high resistance to prevent anode-cathode interactions; using soluble pigments to passivate the surface of the metal; supplying a different anode for the dissolving process.

3.1. *Essential properties of anticorrosive coatings*

Anticorrosive coatings' protection mechanisms have been thoroughly explored, therefore there is a substantial body of literature on the issue [60–62]. Bierwagen [63], identified three primary ways of preventing corrosion that an anticorrosive coating can offer based on the following principles (i) barrier defense (ii) sacrificial/cathodic protection, and (iii) passive/inhibitory defense (coating produced using additives or inhibiting pigments).

3.1.1. *Barrier protection*

As the name suggests and as illustrated in Fig. 4a, barrier protection relies on the construction of a barrier that will stop the migration of species necessary for corrosion, such as water and oxygen, as well as electrolyte ions (Cl^-, SO_4^{2-}, Na^+, K^+, NH_4^+, and Ca^{2+}) to and from the surface of the metal. It is an essential layer of defense that was initially touted as the primary method of coating protection. However, its oxygen and water permeability rendered it ineffective[64]. It has been established that the amount of oxygen and water delivered through the coating was at a factor of 10 larger than or equivalent to the amount required to aid corrosion [64,65]. It is important to consider the resistance to charge flow while considering the obstruction to the movement of electrolyte ions [60]. When electrolyte ions are delivered to the interface, they may interact with metallic species to generate soluble complexes that will dissipate from the places of corrosion and encourage the corrosion cycle [66]. For this reason, it is essential that ion-free water is the water allowed to diffuse through the coating. According to Mayne, the ionic resistance of the coating is what determines how much corrosion occurs, however, Sykes et al. [67] recent research demonstrated that there is no undeniable link between conductivity and corrosion prevention. By employing bi-electrodes and electrochemical impedance spectroscopy (EIS), they attempted to quantify the high-resistance channel, but their results demonstrated that this was impossible. They also conducted tests at high temperatures, demonstrating that the coating resistance assessed could not stop the corrosion process. Barrier protection of coating material is known to be highly dependent on a number of variables, including, the polymer layer structure (crosslinking density and thickness), the polymer properties, how it interacts with the substrate, the presence of a pre-treatment layer, pigment volume concentration, type of pigments/fillers, pigments/fillers' particle shape and the type of corrosive environment [59,68]. It is worthy of note that barrier coating can be applied as a primer, an intermediate layer, or a topcoat.

The nature and form of the pigments employed in barrier coating will determine how effectively they can obstruct water and ion movement through the coating as depicted in Fig. 5b. A difficult route will be provided for aggressive species by lamellar pigments as opposed to spherical pigments, which will allow them to travel through coatings nearly directly. The pigments employed in barrier coatings are inert and water insoluble. The accumulation of layers in the dry film is a factor to take into consideration when considering lamellar pigments because more layers provide better protection. The dimensions and shape of the lamella, particularly their diameter-to-thickness ratio, are what regulate this action [59,69]. Materials derived from minerals make up the two major categories of barrier pigments; metallic flakes (aluminum, zinc, stainless steel, nickel, or cupronickel), mica, micaceous iron oxide (MIO), and glass flakes that are made of minerals. Detailed information on various kinds of barrier pigments is well-documented [69–71].

3.1.2. *Sacrificial protection*

For sacrificial coating, the galvanic effect provides protection. A metal or alloy with electrochemical activity greater than the material

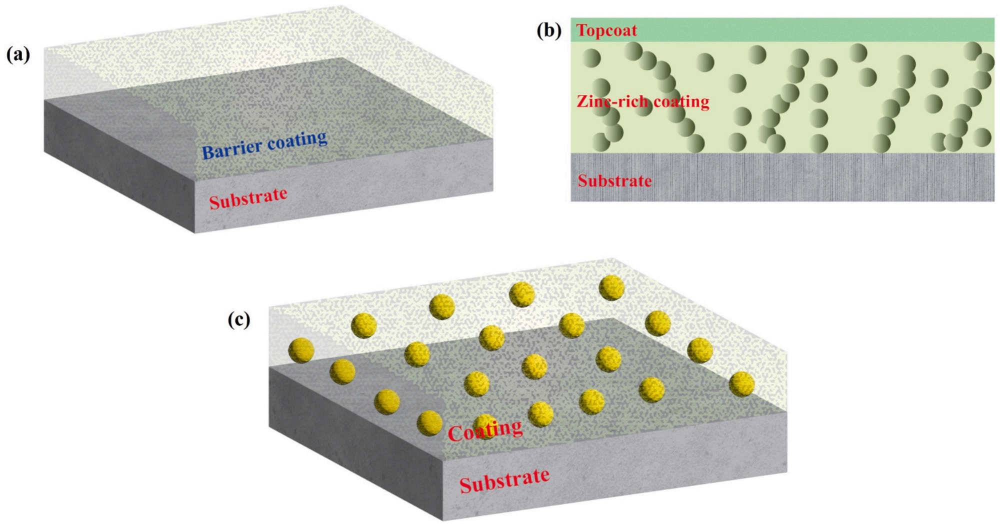

Fig. 4. Coating schemes depicting (a) barrier protection, (b) sacrificial protection by zinc-rich coating, and (c) inhibitive/passive protection.

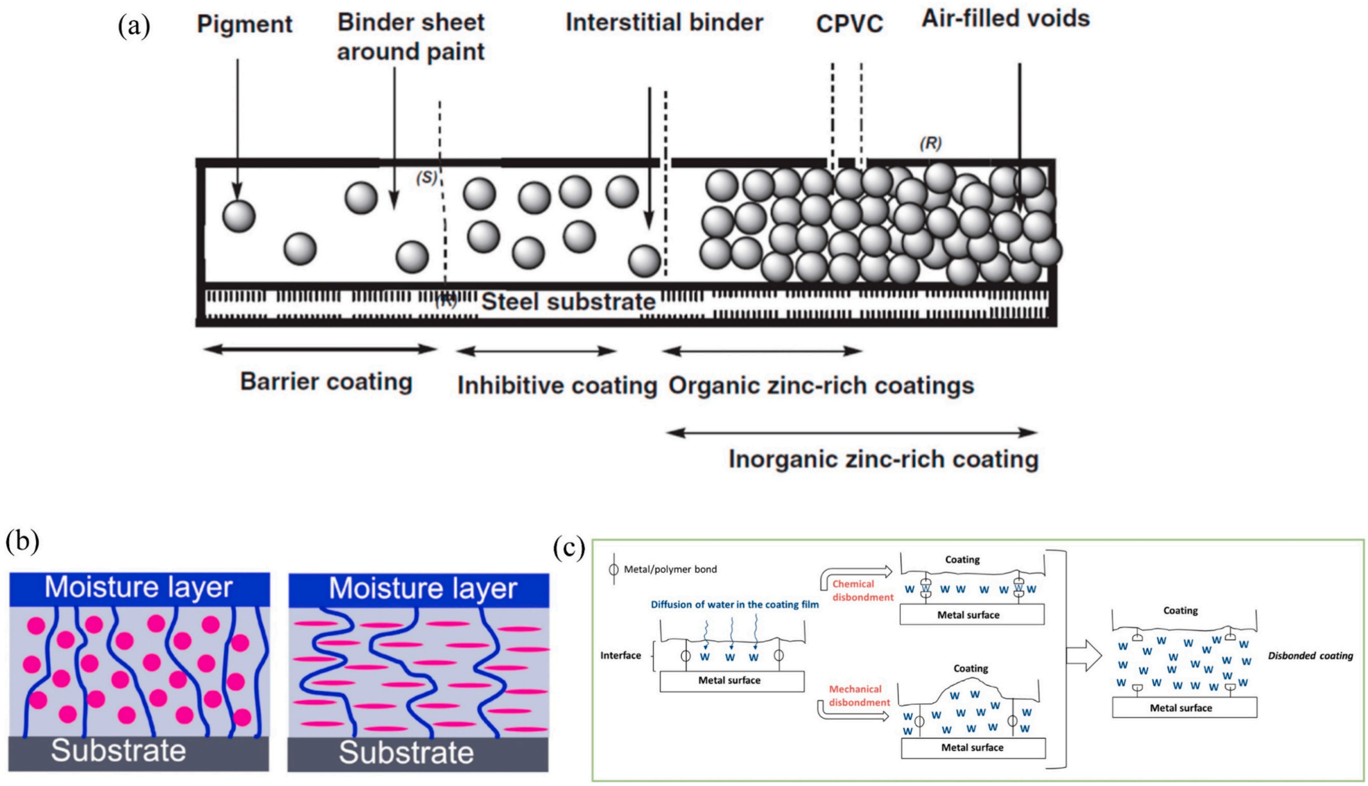

Fig. 5. (a) Pigment volume concentration (PVC) as a function of the type of anticorrosive coating. CPVC stands for critical pigment volume concentration [59]; (b) Barrier properties of shaped pigments: Spherical pigments allow easy percolation of water while lamellar pigments create a tortuous pathway for diffusion [68]; and (c) Water disbonding and adhesion reduction mechanisms [96]

being protected will be used to shield the substrate. In fact, the shielding metal or alloy will dissolve preferentially while the steel remains unreacted. Regarding coating, pigmentation is used to produce cathodic protection. As shown in Fig. 4b, zinc pigments are the main pigments utilized to create sacrificial shielding. For the coating to provide cathodic protection, the quantity of sacrificial pigments must be sufficient to guarantee an electrical connection between them. Steel will be shielded given that the conductivity of the paint is maintained (there are still enough pigments in the paint to function as an anode). For zinc-rich paints (ZRP), the zinc weight in the dry film must be greater than 80%. The size and form of the particles of zinc are other significant factors to be controlled, with size being more crucial.

This form of protection kicks in once the coating is destroyed. It will cause zinc particles to be consumed, and this will lead to the creation of corrosion products. Usually, the accumulation of insoluble corrosion-related byproducts in damaged areas allows the metallic powder to provide barrier protection in addition to cathodic protection. As they precipitate, the corrosion-related by-products clog the coating's pores, lowering the film's permeability [72–74].

Sacrificial coatings are only used as primers because they need to make electrical contact with the steel to be effective, which can only be achieved when the coating is in close contact to the steel. Since these coatings have a low quantity of binder and other components, their other characteristics (including mechanical characteristics, adhesive and cohesive strength characteristics, and impact resistance) are greatly diminished [75,76].

3.1.3. *Inhibitive/passive protection*

Inhibitive/passive protection depicted in Fig. 4c, like sacrificial protection, depends on pigment activity as soon as the surface being protected encounters moisture. Even though the dissolving of inhibitive pigments is the initial stage, their mode of action is distinct from that of sacrificial pigments. Typically, these pigments are chosen for their ability to change into metal compounds or complexes that are insoluble when interacting with the surface of the steel following their partial breakdown due to water seeping through the coating [77]. The insoluble metallic salts passivate the steel as they accumulate thereby preventing the movement of hostile species and serving as a barrier. Inorganic ions with a tepid water solubility make up inhibitory pigments. The most widely used inhibitive pigment is according to the chemistry of phosphates and mostly uses zinc phosphate. Although their effectiveness as a corrosion inhibitor is conflicting, zinc phosphates are known to function effectively in industrial environments because of their limited solubility and lack of activity, which make them suitable for a wide variety of binders [64]. It is also possible to find phosphates made of aluminum, barium, iron, cadmium, calcium, or magnesium. Anodic inhibition, which maintains a passive layer, and cathodic inhibition, which slows corrosion by limiting oxygen passage to the surface, are two examples of inhibitive pigment actions [75]. There are several processes through which zinc phosphates shield steel from damage, and they have all been extensively discussed in the literature [78–81]. Knudsen and Forsgren [78], have meticulously described numerous types of zinc phosphates. The protective processes of other pigments are like those of zinc phosphate. Ferrites, calcium-exchanged silica, barium molybdates, metaborate, and silicates are some of the additional forms of inhibitive pigments that have been highlighted [69,82–85]. Inhibitive coatings require water to dissolve and then operate as a barrier, therefore designing them is tricky because their effectiveness depends on opposing requirements. The efficiency of the inhibitor must therefore be balanced with the barrier qualities. The type of inhibitive pigments used in the layer, as well as their solubility in the organic coating, will determine how much protection an inhibitive/passive layer will provide. Just like sacrificial coatings, inhibitive coatings are applied as primers since they need to react with the steel surface to provide protection.

3.1.4. *Adhesion protection*

As reported by Funke [86], adhesion is the most crucial property of organic coatings, if the adhesion property fails, all other coating properties are rendered useless. He also identified adhesion as a form of protection, alongside barrier protection (Physicochemical mechanism) and pigment protection (electrochemical mechanism) [87]. It is a known fact that adhesion is not mentioned alongside the three postulated methods of protection in most writings about corrosion protection. Although the interactions between atoms and molecules at the intersection of two surfaces can be defined as adhesion, the phenomenon is quite complex and involves knowledge from other fields. As an essential component of the protection provided by coatings, adhesion has been the subject of several research to describe, and explain how it operates, and demonstrate how to predict it [88–92]. There are several theories that attempt to explain adhesion, but the goal here is not to evaluate them; further details can be obtained elsewhere [93,94]. By delaying the production of corrosion products, hydrogen evolution, and water accumulation under the coating, extremely strong adhesion can aid in the suppression of corrosion. Adhesion basically serves to establish the circumstances necessary for corrosion prevention mechanisms to function. In fact, an organic coating cannot serve as a passivation layer, provide a route of extraordinarily high electrical resistance at the metallic surface, or keep in touch with the electrolyte or corrosive species from occurring without close contact with the metallic surface at the atomic level. Nevertheless, adhesion is just “essential but insufficient” for effective corrosion protection. Since improved corrosion protection is not always implied by good adhesion, protection cannot be ensured by adhesion alone [95]. This is especially true when evaluating dry adhesion, the bond’s initial strength between the coating and substrate. Dry adhesion has been reported to be less important than wet adhesion in terms of protecting against corrosion [86]. Wet adhesion is the attachment of an organic coating to a substrate after contact with liquid water or a lot of humidity. Wet adhesion is a property of coatings, not a mechanism for failure. The identical polar groups on the molecules of the binder that promote strong dry adhesion might also lessen water repellency at the coating-metal contact and, consequently, the wet adhesion. Leidheiser and Funke [96] proposed two disbonding mechanisms based on their review of the literature: the mechanical disbondment caused by water building up at the interface and the chemical disbondment where the water molecules can disturb the interactions between the polymer and the metal oxide as depicted in Fig. 5c.

Overall, the mechanisms of adhesion are governed by the physical and chemical properties of the metal (quality of reactive species and their spatial placement on the surface of metallic, roughness) and the polymer (chemical composition and spatial placement of the components, and mechanical properties, rheology, glass transition temperature (Tg),). Therefore, drawing conclusions about the function of adhesion is challenging since it can be viewed both as a protection and as a prerequisite for corrosion protection to function. However, this coating quality is crucial and must be properly considered.

3.2. *The role of nano/microcontainers in enhancing coating performance*

One of the latest inventions in improving coating performance is the introduction of nano/microcontainers, in the advanced field of nanotechnology. This has since matured quickly with exciting outcomes. These containers can be filled with substances which are released when they experience excitation or trigger, and in turn accomplish their intended mission such as corrosion healing, anti-fouling, cancer therapy, cement healing, etc. [97,98]. These nano/microcontainers are typically preloaded with various forms of corrosion inhibitors and are usually made in containers or reservoirs such as $CaCO_3$ microbeads, TiO_2 nanocontainers, carbon nanosheets, polyelectrolyte nanocapsules, chitosan microspheres, silica/Lacithin, CeO_2 hollow spheres and Eudragit polymeric particles, among others [35]. In addition, a comprehensive summary of nano/microcontainers, the incorporated active inhibitors and the assessment technique when used in active anticorrosion coatings has been previously presented by Udoh and coworkers [6].

In their course of activity as shown in the schematic representation of Fig. 6, these containers function as reservoirs by storing the functional species until the time of their release, which is activated by different types of stimuli, and then releasing them only at the onset of the damage to the coating, thereby immediately self-healing the defective area [3,6,35]. Moreover, it is important that these containers should adequately possess good compatibility with the coating matrix. They must also be stable and have the capacity to store the active inhibitive agents for a long time, so that they can be released when required. This system is also adopted in developing multifunctional protective coatings that are both anti-fouling and bactericidal [99].

4. Integration of nano/microcontainers into anticorrosive coatings

4.1. *Strategy for incorporating nano/microcontainers into coatings*

Due to the potential to enhance the functionality and effectiveness of coatings, the incorporation of nano/microcontainers into coatings is

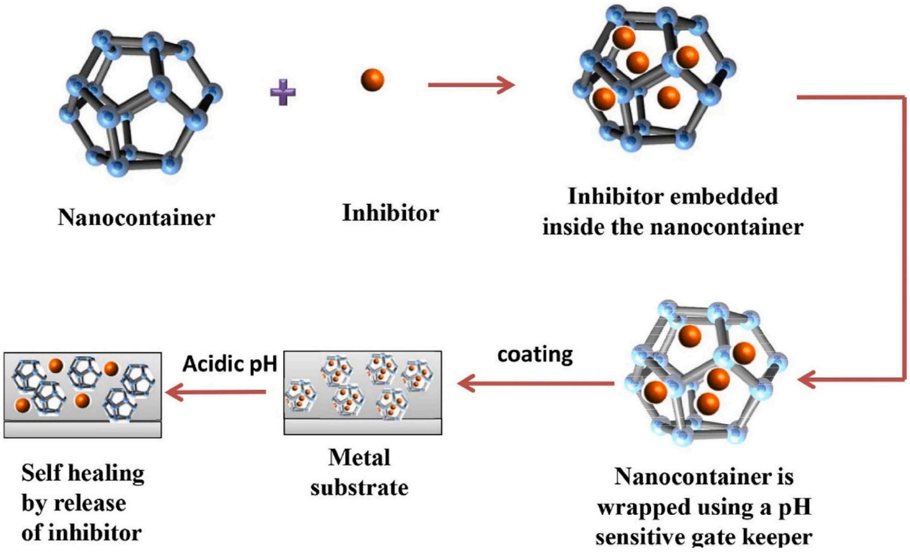

Fig. 6. Schematic representation of the mechanism of nano/microcontainers [35].

important [100,101]. Controlled release, targeted distribution, and increased durability are problems that can be solved by nano/microcontainers, which can encapsulate and release active substances. Usually, utilizing the direct mixing technique, these synthesized nano/microcontainers may be effectively included into coatings matrix.

Direct mixing during formulation involves mixing the coating formulation directly with nano/microcontainers while it is being prepared [102]. The coating matrix can accommodate the dispersion of the containers, resulting in a uniform distribution of the coating. Udoh et al. [3] prepared different coatings by integrating the microcontainers into the resin. In another work, after 30 min of stirring, a uniform dispersion was attained with 0.5 wt% of microcontainers placed directly into the epoxy resin during formulation [103]. Njoku et al. [104]used a two-blade mechanical stirrer to combine 5 wt% of microcapsules in a 3:2 weight ratio with the epoxy resin (E44 epoxy) and the curing agent (polyamide TY-650) for 40 min, respectively. Also, by adding 5 *w*/w% of the nanotubes to an epoxy coating slurry, Njoku et al. [105] synthesized coatings, then agitation (sonication) and stirring were used to separate the nanotubes and distributed them equally throughout the coating matrix. The distribution of nano/microcontainers within coatings plays a role in the performance of the coating. Research on the impact of where the coating's nano/microcontainers are placed has revealed that coatings with containers near the metal surface offer superior corrosion protection compared to coatings where the coating layer with containers is separated from the protected surface by a second layer that lacks containers [106]. Nevertheless, agglomeration problems and concerns with coating compatibility with containers must be carefully considered notwithstanding the benefits achieved by including containers in the coating matrix. Thus, the suitable combination of starting materials and fabrication procedures can be chosen to develop microencapsulated products with a wide variety of compositional and morphological characteristics.

4.2. Effect of container properties on the anticorrosive behaviour of coatings

The anticorrosive performance of protective coatings is significantly improved by nano/microcontainers, which are utilized as carriers for active agents in coatings. These containers create a controlled release system inside the coating matrix by encasing and discharging corrosion inhibitors. These nano- and microcontainers' characteristics greatly affect how well they prevent corrosion for a long time [107]. The properties of the container are used to illustrate how coatings' ability to resist corrosion is affected.

4.2.1. Container size and morphology

The size and form of nano/microcontainers have a significant impact on the anticorrosive properties of coatings. Greater barrier characteristics and prolonged inhibitor release are provided by smaller containers with high aspect ratios because they spread more evenly inside the coating [108]. Additionally, when microcapsules are incorporated into coatings, the capsules' elastic stiffness, fill content, and burst strength are the crucial factors for the effective administration of the healing agent. The size of microcapsules can be regulated by the surfactant concentration [109], stirring speed [110], temperature, and time [111,112] during fabrication. Furthermore, this kind of microcapsule has been reported to possess a rough outer surface which makes it possible for adhesion improvement, when embedded into the coating system [112]. The roughness of the outer surface morphology contributes to enhancing the adhesion between the host coating matrix and the microcapsule by boosting contact interfacial area with the matrix material [113]. Additionally, the roughness on the surface of the microcapsule will cause tension concentration, making breakage very easy [112]. Consequently, it was found that coatings doped with smaller containers perform better in with regards to self-healing.

4.2.2. Container material

The material composition of nano/microcontainers is a key determinant of their anticorrosive effectiveness. The performance of self-healing is significantly influenced by the characteristics of the container and how it reacts to external stimuli [114]. The membrane of the container is such that it possesses some sort of blocking effect between the surroundings and the internal phase. The outer sheath tends to rupture or expand in response to the matching stimulation, reducing its surface density and releasing the core contents to alter external conditions or react with specific substances outside. A typical microcapsule, for example, consists of a solid polymeric shell and a liquid/solid core material. When a microcrack originates from internal stress (due to the accumulation of corrosion products in the coating matrix) or physical damage (scratch) through the coating, because of capillary stresses, the microcapsules are meant to burst and release healing agents that flow to the defected plane. Then, the healing agents begin to work together to create a polymer network that seals the defect. Material preservation and isolation can be achieved for extended periods of time using microcapsules that are highly durable and have walls that are robust but not so strong as to burst on demand. However, new findings imply that the parameters associated with the encapsulation process have a significant impact on the durability of the capsules, which raises the possibility that creating long-lasting microcapsules may be more challenging than anticipated. Sun and Zhang [115] investigated the mechanical strength of microcapsules with walls composed of urea-formaldehyde resin, melamine-formaldehyde resin, and gelatin-Arabic gum. In a similar development, a multilayer microcapsule shell production has been described [116]. Microcapsules must be solvent-resistant, easily dispersed without being destroyed, able to burst open upon coating cracking, and able to release the healing agent to be used in coating systems [117]. To ensure the suitability of the microcapsules for use in coatings they are characterized to determine the mechanical stability, core size, wall thickness, surface morphology, particle size distribution, analysis of the capsule contents, viscosity of the capsule contents, and storage stability. This redox-responsive corrosion reaction (opening and closing) of a polymer shell and its containing active species has been demonstrated [118]. Along with all the benefits of microcapsule design, the pH-sensitive release microcapsule architecture offers a real controlled-release function for corrosion applications. pH-sensitive microcapsules release their contents when corrosion starts, as opposed to typical microcapsules, which release their active agents during mechanical rupture. In this mechanism, for achieving release via diffusion, the thickness and deformation of the membrane play a vital role and for core materials, the solubility, diffusivity, and partition coefficient are critical [119–121]. Mechanical damage of coatings is one of the essential causes of corrosion of the base metal. However, several forms of defects in coatings, such as uneven thickness, air bubbles, porosity, permeation, or edge effects, will likewise cause the coating's corrosion protection to be inadequate and permit corrosion to happen. Regardless of the corrosion caused, pH-sensitive microcapsules will release their substance for corrosion detection or prevention. Several researchers have proposed the use of pH-sensitive polyelectrolyte shells outside loaded micro- or nano-containers to control the release of the embedded self-healing agents and inhibitors [122,123]. Due to their excellent chemical stability and compatibility with coatings, inorganic materials such as silica, zeolites, or clay nanotubes are frequently selected. Another option is to use organic polymers, although their long-term usefulness may be hampered by degradation under corrosive conditions.

4.2.3. *Container loading capacity*

The quantity of inhibitor that nano/microcontainers can encapsulate, or their loading capacity, affects the coating's overall performance. The employment of intelligent nano-containers that are packed with inhibitors has increased the lifespan of anti-corrosion coatings and reduced the rate of metal corrosion. The inadequate loading capacity of the inhibitors limits the uses of the nano-container [114,124,125]. While exceeding the capacity could result in an early exhaustion of the inhibitors, high loading capacities allow for a sustained release of the inhibitors [126,127]. The explanation for this phenomena is that the high concentration of microcapsules caused more diffusion channels to be introduced at the microcapsule-coating interfaces, which in turn compromised the integrity of the coating matrix [128]. It has been reported elsewhere that the morphology of the microcapsule shell plays a major role in the rate of release [129]. Higher adhesion strength is maintained at optimal doping levels, and it is critical to balance loading capacity with desirable release kinetics.

5. Functionalities provided by porous nano/microcontainers in multifunctional anticorrosion coatings

Coatings with more than one protective function can be defined as multi-functional coatings. Porous nano/microcontainers have played vital role in the development of multi-functional coating technology [130]. Several dye or indicators[131], corrosion inhibiting agents [132,133], polymeric self-healing agents[134],and biocides[135,136] have been encapsulated in these containers and doped into several coating systems for early detection of corrosion, inhibition, self-repairing of damaged coating matrix and antifouling properties, respectively. Also, low surface energy materials have been mixed or anchored on nano/microcontainers to afford water-repelling properties [137]. This extension of the protection prowess of anticorrosion coatings is important for the protection of structures deployed in different environments. The invention of multifunctional coatings i.e., active and self-healing coatings over the past decades has paved way for the development of several approaches to extend the service life of different coatings used in both organic and inorganic based anticorrosive coatings, thereby reducing the maintenance cost in different industries (for example aviation, civil, oil and gas, automobiles and lots of structural parts of civil and construction engineering facilities). The greatest aspect that has received attention is the ability of nano-porous and micro-containers to anchor several self-healing agents (polymer, catalyst, corrosion inhibitors) on/in their pores and to deliver them on-demand. In this regard, different micro/nanocontainers such as carbon nanotubes [138,139], mesoporous silica[140–142], clay nanotubes (hallysite) [143–146], TiO_2[140–142], metallic oxide nanocontainers[147,148], etc. have been utilized. These nano/microcontainers provide excellent large surface areas, stability, pore volume, etc. that favours the encapsulation and/or anchoring of various healing agents useful in the engineering of multifunctional coatings. These capabilities have evolved into different kinds of multifunctional coatings such as self-repairing coating, Uv-resistance coatings, etc. However, the simplicity of inorganic nano/microcontainers eliminates the tedious encapsulation process involved in other kinds of microcontainers such as polymer nanocontainers.

5.1. *Controlled release of corrosion inhibitors*

The controlled release of corrosion inhibitors from nano/microcontainers is an important aspect of corrosion studies that explain the effectiveness of smart carriers. Aside from other forms of corrosion mitigation methods [149–155], smart nano/microcontainers with corrosion inhibitors are often adopted partly because of their controlled release of inhibitor functionalities.

Due to the need to mitigate and control the environmental concerns arising from metal corrosion, the use of corrosion inhibitors associated with smart nano/microcontainers has become pertinent. The essence of adopting these peculiar corrosion inhibitors within matrixes of carriers is a result of the stimuli-responsive functions compared to other forms of inhibitor systems. The buildup of the smart functionalities is sometimes linked with the controlled release of corrosion inhibitor components and self-healing materials from the coatings [156,157]. According to Chen et al. [158], the stimuli response mechanisms regulating the release of corrosion inhibitors from nano/microcontainers can broadly be classified as (I) endogenous; pH, redox and ion-exchange, and (II) exogenous; Temperature, magnetic field, and light, as depicted in Fig. 7. In a work by Tian et al. [159], the use of Zn–Al–NO_2 layered double hydroxide (LDH) as a controlled-release inhibitor for steel reinforcing in concrete contaminated with chloride was demonstrated. The total amount of nitrite released by LDH was observed to be affected by the chloride content in the solution. However, it is worthy of note that two or more conditions can stimulate the release of inhibitors from nano/microcontainers. For example, in a study carried out by Li et al. [160], corrosion inhibitor molecules were released under control when hollow mesoporous organosilica nanocontainers were subjected to pH and redox dual stimuli-responsive conditions.

5.2. *Improved adhesion and self-healing barrier properties*

Emerging trends exist that narrate the various applications of the improved adhesion and barrier properties made possible by nano/microcontainers in multifunctional anticorrosive organic coating [161,162]. In a work by Qian and coworkers [163], a mussel-inspired characteristics of dopamine was used to achieve improved barrier

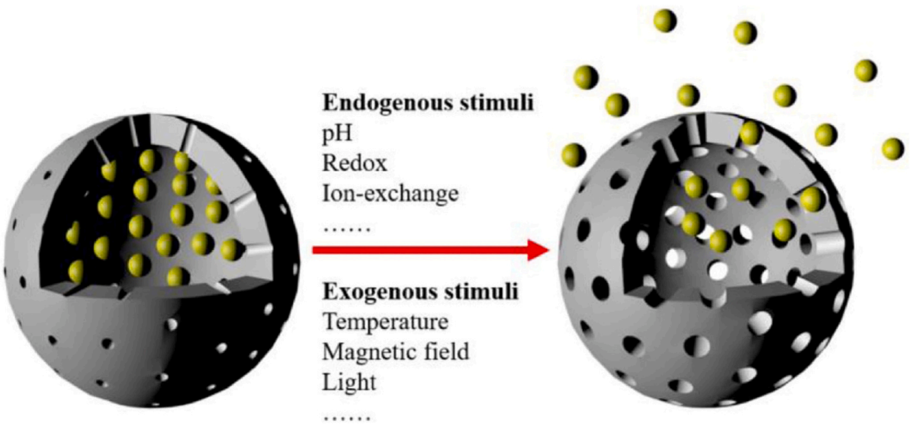

Fig. 7. Stimuli response of smart nano/microcontainers [158].

coating associated with nano/micro-containers. As schematically represented in Fig. 8a, the increased potential of dopamine groups to increase the adhesion of nanoparticles to smooth surfaces was employed to achieve better adhesion in the coating. Fig. 8a also depicts the profiles obtained from the release of inhibitor benzotriazole (BTA) from mesoporous silica nanocontainers (MSNs) at pH 2, 5, and 7. The research proved that the coatings incorporated with benzotriazole derivatives exhibited promising self-healing characteristics. The profiles of impedance modulus at 0.01 Hz ($|Z|_{0.01\text{Hz}}$) shown in Fig. 8b reveal interesting insights into the development of functionality within the different scratched coatings under examination. The corrosive species gradually seep into the coatings' scratches as immersion times rise, which causes the impedance modulus of the blank coating and coating with empty MSNs to steadily decline. After a day of immersion, the coating doped with MSNs-BTA (Fig. 8b, curve 3) had the largest $|Z|_{0.01\text{Hz}}$ (1.0×10^6 Ω cm^2). Shortly after the sample is submerged, the inhibitor's rapid release may prevent corrosion from starting. However, after 5 days of immersion, the $|Z|_{0.01\text{Hz}}$ shows a dramatic decline from 1.0×10^6 to 2.4×10^5 Ω cm^2. The release profile (in Fig. 8a) demonstrates that BTA leakage from MSNs-BTA may take place in a neutral solution. The entire testing region might see a direct release of BTA. It is previously known that directly doping the coating with the corrosion inhibitor may have an adverse effect on the adhesion of coating to the steel, or compromise the integrity of the coating matrix, hence reducing the coating's ability to protect against corrosion. After 1 day of immersion, the $|Z|_{0.01\text{Hz}}$ for the coating made with MSNs-BTA@PDA is still lower than that of the coating made with MSNs and MSNs–BTA. This is most likely because the surface of MSNs-BTA@PDA still has hydroxyl groups, which can encourage water to seep into the coating. After 20 days of immersion, the coating containing MSNs-BTA@PDA exhibits a sustained resistance rise over an extended period, rising from 8.3×10^4 to 7.0×10^5 Ω cm^2 (Fig. 8b, curve 4). Other coatings under investigation did not exhibit this kind of self-healing behaviour. The scratched area is sustainably protected by the on-demand release of BTA from the nanocontainers. Fig. 8c

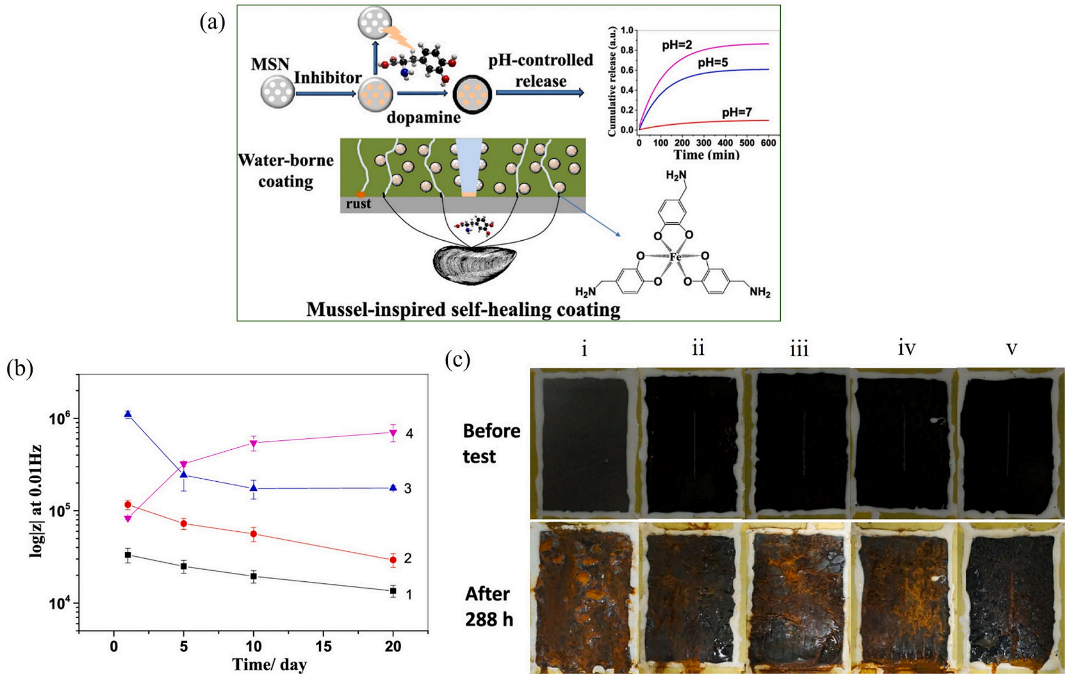

Fig. 8. (a) A scheme of mussel-inspired self-healing coating for improved adhesion and profiles of benzotriazole (BTA) release from mesoporous silica nanocontainers (MSN) at different pH values; (b) Impedance modulus at 0.01 Hz for scratched coating during immersion in 0.1 M NaCl for (1) blank coating, (2) coating with MSNs, (3) coating with MSNs–BTA, and (4) coating with MSNs–BTA@PDA; (c) Photos of mild steel surfaces before and after 288 h of immersion in salt spray chamber: (i) bare mild steel, (ii) blank coating, (iii) coatings with MSNs, (iv) coatings with MSNs–BTA, and (v) coatings with MSNs–BTA@PDA [163].

displays photos of mild steel and mild steel covered with various coatings both before and after 288 h of salt spray tests. Accordingly, mild steel with coating containing MSNs-BTA@PDA performed better, demonstrating their improved barrier qualities and capacity for self-healing. These outcomes attest to the enhanced anticorrosion properties of coating doped with MSNs-BTA@PDA nanocontainers [163]. By applying the mussel-inspired chemistry on nano/microcontainers, several other works have demonstrated improved adhesion of coating [164–167].

Nano/microcontainers have also found wide application in the improvement of barrier properties of organic coating [106,111,168–172]. For example, a coprecipitation approach was used to synthesize inhibitor nanocontainers with a two-dimensional (2D) structure utilizing graphene oxide and layered double hydroxides (GO/LDHs) [173]. An anion exchange procedure was used to load the corrosion inhibitors of vanadate anions (VO_x^-) and 2-mercaptobenzothiazole anions (MBT^-) into the GO/LDHs nanocontainers while maintaining the 2D structure of the end products. Their incorporation into a sol-gel coating on AA2024-T3 showed significant protection. Two factors were identified as contributing to the improvement of the protective properties: the corrosion inhibition of vanadate anions and the excellent barrier of GO sheets, as well as the good dispersion of the additive with the 2D structure. Nano/microcontainers have been very effective in modulating the barrier properties of coating since they play a pivotal role in releasing inhibitors and sometimes trapping the chloride ions. Moreover, it was shown that the smart coating having phosphate anions, vanadate, and other anions had a synergistic anticorrosion influence on metal [99].

Typically, corrosion process is associated with pH changes in the anodic and cathodic sites of the metal. Materials that are pH sensitive have been employed to achieve self-healing. Polyelectrolyte swelling and crosslinking reactions, and the corrosion inhibitors performance are pH sensitive. These have been explored to achieve self-healing in protective coatings. Persistent release into the environment has encouraged the development of systems that can contain the active agents and release them at the onset of corrosion reaction. Therefore, the coatings must possess the ability to detect environmental changes akin to the onset of corrosion and respond autonomously to release self-healing agents. The continuous release of self-healing agents has been criticized due to short life span and environmental pollution. Secondly, it can only offer minimal and short-term protection. To advance the protective lifespan and minimize environmental release, researchers are focusing on developing systems which interface nano/microcontainers with polyelectrolytes sensitive to corrosive entities like pH, ionic strengths, pressure, and water, etc., so that the coating system can release inhibitors on demand, withhold it back after the taming of the corrosion action and then repair any mechanical damage. This is achieved by re-enveloping or interfacial deposition of self-repairing polyelectrolytes on the nanoparticles. There are different categories of self-healing coatings provided by different researchers with the aid nano/microcontainers. Coatings doped with containers which provides only active protection (due to the release of self-healing agents) are best described as active coating whereas coatings that release self-healing agents only when triggered and withhold them afterwards are described as smart coatings, while coating with additional ability to self-repair mechanical damages on the coating to reinstate barrier properties are described as self-repairing coatings. As shown in Fig. 9a, common examples of nano/microcontainers used for active and self-healing purposes include LDHs, halloysite, mesoporous silica, and diatomaceous earth. The inhibitor loading process and overall functionality is critical in the performance of these nano/microcontainers. For example, inhibitors can be loaded in the shell of nanocontainers during a layer-by-layer (LbL) assembly of oppositely charged polyelectrolytes grafted on the surface of zinc oxide core, as demonstrated in Fig. 9b [174]. Also, dendritic silica nanocontainers were employed to entrap L-histidine (L-His) and Zn^{2+} ions in the core. The loading and release of these inhibitor components prevented their direct interaction of the coating components, and their release can be triggered by water ingress and/or corrosion reaction onset [175]. Fig. 10a shows a scheme of the synergistic corrosion protection mechanism of the HZK/Ep coating containing nanocontainers based on dendritic silica (KCC-1), L-histidine (L-His) and Zn^{2+} ions, and Fig. 10b reveals the superior performance of the nanocontainer-incorporated coating indicated by highest impedance after 40 days of exposure to 3.5 wt% NaCl solution. The potential of functionalization and incorporation of nano/microcontainers has led to a generation of coatings with improved self-healing properties.

Moreover, corrosion and associated changes in the local pH are among the factors that typically influence the design of self-healing systems. Corrosion is an integral part of an electrochemical phenomenon since it occurs with electron production and transfer between a

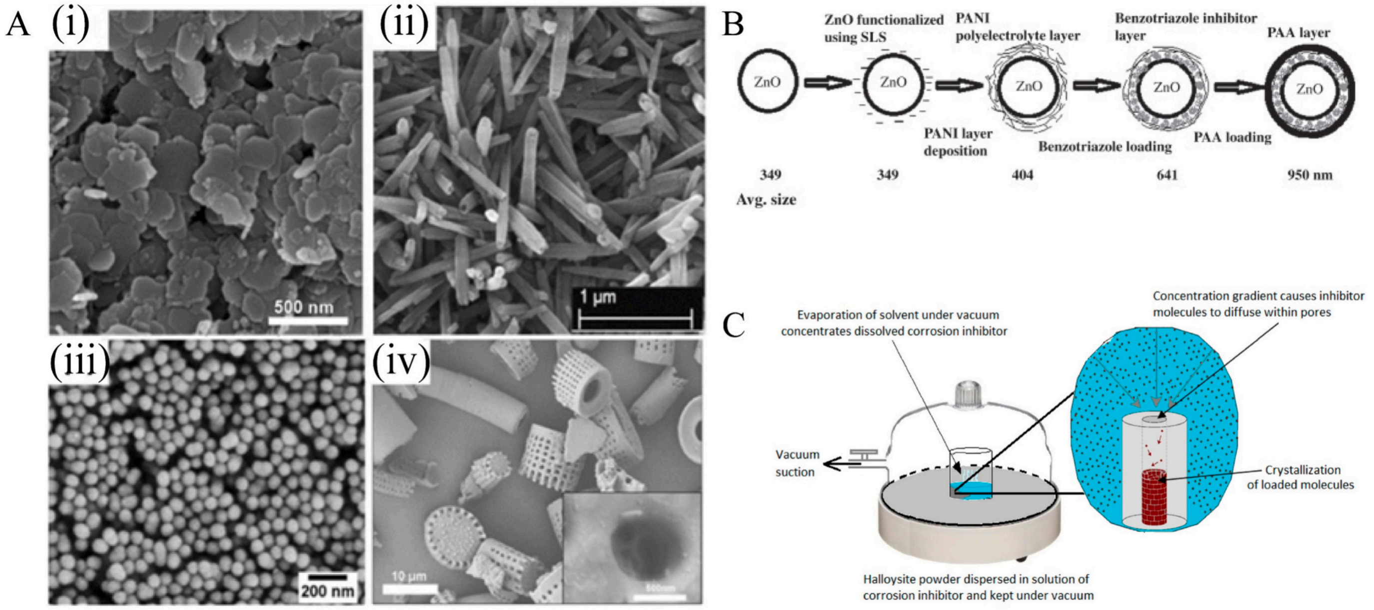

Fig. 9. (a) Typical nano/microcontainers for multifunctional coating application [131,176]: (i) LDHs, (ii) halloysite, (iii) mesoporous SiO_2 and (iv) diatomaceous earth; the inhibitor loading of (b) hard core [174] and (c) porous or hollow core [177] nanocontainers.

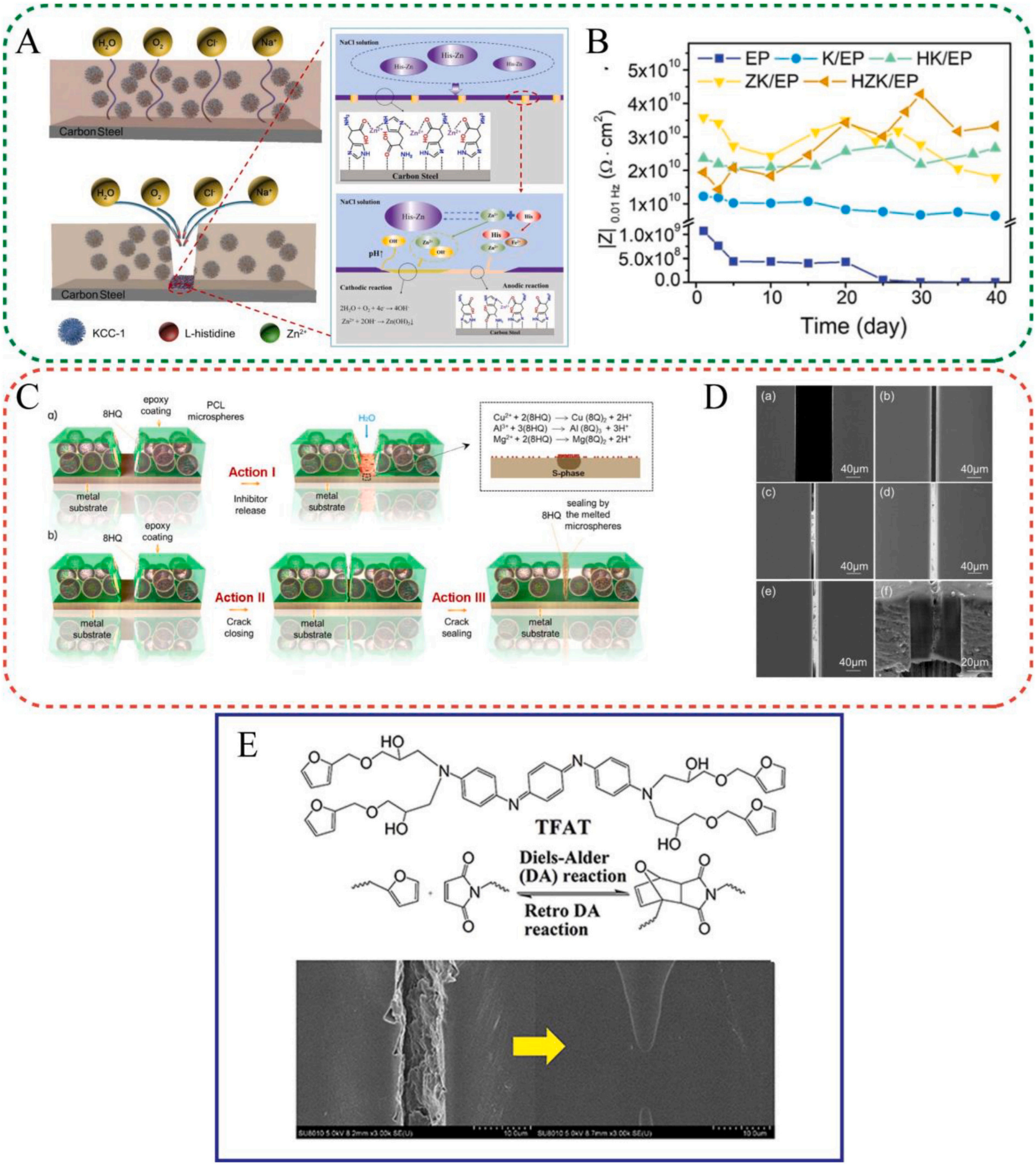

Fig. 10. Typical active and self-healing mechanisms: (a, b) inhibitor release for active protection [175]; (c, d) inhibitor release and crack sealing for multifunctional active and self-healing protection [178]; and (e) self-repairing by polymers for self-healing protection [179].

metal surface and an aqueous electrolyte solution. In near neutral conditions for instance, iron corrosion is consistent with electrochemical reactions as shown in eqs. 1-2:

Cathodic reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4e^- \quad (1)$$

And anodic reaction:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (2)$$

In protective coatings, this sort of corrosion reaction happens in the micro-defects in the coatings, which is synonymous to pitting in metal corrosion process (see Fig. 11a). Hence, the anodic reaction system occurs in the confined micro-defect in the coating and precipitated corrosion products such as iron (II) oxide, $Fe(OH)_2$, (which can be further oxidized to iron (III) oxide, $Fe(OH)_3$), accumulates in the micro-defects[131]. The products accumulation foments the buildup of hydronium ions, H^+ inside the micro-defect at the anodic sites, whereas OH^- accumulates in the cathodic sites. The overall effect of these processes is local pH change. Since corrosion reaction is associated with pH and other electrochemical changes, materials that are pH or otherwise electrochemically sensitive are expected to guide in the detection and control of corrosion. Thus, the local pH change in the micro defects of coatings have been exploited to develop smart coatings[180] with ionic strength and water sensitivity [144] (Fig. 11b), pH responsive [145] (Fig. 11c), and combined pH sensitivity and self-repairing by polyelectrolytes in a typical multifunctional coating [181] (Fig. 11d). Recent

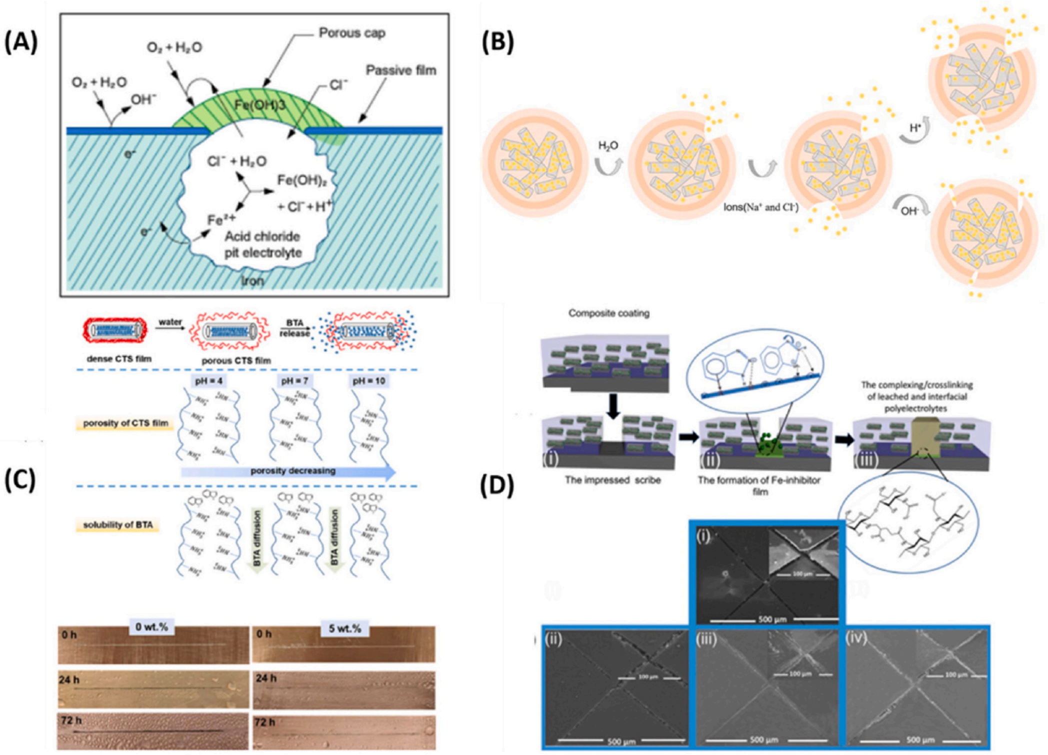

Fig. 11. Mechanisms for (a) pH local change in defects [131], (b) water and ionic strength sensitive capsule [144], (c) pH sensitive inhibitor release in self-healing coatings [145], and (d) pH sensitive combination of inhibitor release and self-repairing by polyelectrolytes process in a typical multifunctional coating [181].

advances in the fabrication of multifunctional coatings from nano/microcontainers are summarized in Table 2.

5.3. Nano/microcapsule in antifouling coatings

Biofouling on surface coatings limits the performance of coated installations submerged in wet environments[190]. And biocides-based antifouling coatings have been the primary strategy for combating biofouling in marine and offshore industries till present [191,192], because the seemingly “green” fouling release antifouling coating system (i.e. fouling resistant super-hydrophobic coatings) still lacks applicability. Nano and micro-particles have contributed to the successes of the developments of these functional coatings[193]. Fig. 12a demonstrates how antifouling agents anchored on nanoparticles could lead to antibacterial effects. Deng et al. fabricated a coating embedded with antibacterial nanoparticles. The particles were functionalized with terpolymer to afford combined synergistic antibacterial and antifouling coating embedded with nano-composite Ag@TA-SiO_2 particle[194]. It is also possible to contain biocides in/on nanoparticles and disperse in conventional coating matrix to achieve antibacterial effect. As shown in Fig. 12b, Njoku et al. fabricated multipurpose epoxy coating using antibacterial chitosan cross-linked with glutaraldehyde to produce pH sensitive dissolution and release of protonated chitosan and modified epoxy coating for combined self-healing and antibacterial effects[181]. Mohan et al. achieved antifouling paint formulations with ZnO and Fe_2O_3 nano-paints for marine applications[195]. They found that both fouling and antibacterial properties can be reduced with an increase in the concentration of nanoparticles. Alarif et al. [196] synthesized TiO_2 using a biological marine natural algae extract. The introduction of the synthesized nanoparticles into coating formulation impacted excellent antifouling effects. Other nano/micro-particles that have been employed in antifouling coating fabrication include graphene oxide/silver nanocomposites[197], cerium dioxide (CeO_2-x) nanoparticles [198], etc.

5.4. Self-cleaning coatings

Self-cleaning surfaces and coatings are attracting attention. Such surfaces or coatings have found application in different areas ranging from glass windows, automobile windshields, textiles, building and construction materials, as well as optoelectronic devices, etc. [199]. Mostly TiO_2 based materials have found application in the fabrication of self-cleaning surfaces [199]. Other ways to achieve self-cleaning are in super-hydrophobic materials. Hydrophobic surfaces repel water and dirt as well. When the surface is tilted the water droplet rolls over the surface, picking up dust and moving it away from the surface[200]. Nanomaterials have been useful in the fabrication of super-hydrophobic materials, although their application here may be connected more to surface properties rather than the porosity of the nanomaterials. This technology often relies on low surface energy material functionalization of SiO_2 nanoparticles and different polymeric low surface energy agents have been used to achieve this[201,202].

6. Performance evaluation of anticorrosive coatings with porous nano/microcontainers

Modern laboratory equipment is used for both in-situ and ex-situ evaluation of the performance of anticorrosion coatings in different testing conditions. In most cases, the evaluation procedure (experimental design) is very challenging, hence, it must be carefully planned to achieve the desired results. For instance, various environmental conditions that can affect the performance of coatings during actual use are always predicted and simulated; such conditions include alkaline/acidic, aqueous/nonaqueous, temperature, pressure, etc. Computer simulation tools can be employed to evaluate the performance of coatings where it is difficult to replicate the actual environmental conditions during testing. In this section, the applications of the most prominent techniques in relation to the use of porous nano/microcontainers in the corrosion mitigation process shall be discussed.

Table 2
Different nano/microcontainers for multifunctional coating application.

S/N	Multifunctional coating type	Nano/ microcontainer	Findings	Ref (s).
1	Active	Silver nanoparticles	pH-responsive adsorption of PDMAEMA onto the AgNP was employed to provide pH sensitivity of the coating	[182]
2	Smart	Mesoporous silica nanoparticles	Mesoporous silica nanoparticles were successfully functionalized with Eriochrom Black T (ECBT) which can be released in response to ambient pH changes. This was doped in sol-gel coating to afford the protection of Zr pretreated mild steel n 3.5 wt% NaCl medium.	[183]
3	pH sensitive	Mesoporous silica nanoparticles	Amino-modified mesoporous silica nanoparticles (MSN-NH_2) afforded pH responsive delivery of benzoic acid inhibitors thereby making the acrylic matrix doped with the functionalized and inhibitor loaded microcapsule to offer smart protection of Al alloy.	[184]
4	Smart	Micron size calcium carbonate beads	$CaCO_3$ microbeads dissolve in low pH conditions akin to corrosion onset which can permit the release of loaded inhibitors	[148]
5	Self-repairing	Halloysite nanotubes	The nanotubes (HNTs) was loaded with $NaNO_3$ as an inhibitors and thereafter re-encapsulated with urea formaldehyde microcapsules containing self-healing agent (linseed oil (LO)). The dispersal of the functionalized capsules in coatings afforded self-repairing of inscribed defects as well as pH responsive release of corrosion inhibitor.	[185]
6	Composite coating	MWCNTs/TiO_2	The distribution of the nanoparticles enhanced the adhesion strength and the thermo-reversible self-healing polymeric matrix.	[186]
7	Self-repairing	Titanium nitride nanoparticles (TiN NPs)	Poly (ε-caprolactone) (PCL) microspheres, with surface covered titanium nitride nanoparticles (TiN NPs) induced photo-thermal heat generation which can cause the melting of PCL polymer causing self-repairing by polymer memory effect of epoxy	[187]
8	Self-repairing	Layered double hydroxide (LDH) carriers	An inhibitor (2-mercaptobenzothiazole (MBT)) was loaded into (LDH) carriers and mixed into an acrylate polycaprolactone polyurethane-based shape-memory coating. This formulation afforded combined self-healing and active corrosion protection of hot-dip galvanized steel (HDG) due to the release of the inhibitors and the shape memory effect of the polymer matrix.	[188]
9	Photothermal, heat preservation and anticorrosive	Nanoparticles based on copper sulfide decorated with polyethylene glycol (PEG@CuS)	A polydimethylsiloxane coating with photothermal heat preservation was fabricated using PEG@CuS phase change nanofillers. CuS nanofillers in the composite coatings produce heat by solar energy, and PEG stores heat through phase shift.	[189]

6.1. Electrochemical techniques

Corrosion monitoring involves the assessment of the different types of corrosion occurring in each environment and the evaluation of the key factors affecting the corrosion rate and propagation. Therefore, electrochemical techniques provide good insights into material corrosion, especially for short experimental duration.

6.1.1. Voltammetry techniques

Voltammetry involves investigating the feedback obtained from a chemical current when a potential difference is applied. It is a general name given to various potential sweep methods used in the study of electrochemical reaction processes taking place in electrochemical systems. Voltammetry methods involve scanning the working electrode's potential in both anodic and cathodic routes at varying scan rates, which covers an expanded range of potential windows while recording the resultant current. The plot of the current with respect to the applied potential is commonly referred to as a Voltammogram (Fig. 13a). The potential sweep technique is very useful in analyzing the thermodynamic (for example, reduction or oxidation potentials) and kinetic characteristics (like rate constants, coefficients of diffusion, participants electron number, etc.) of the electrochemical reactions [203]. The voltammetry method uses a three-fold electrode system; a reference electrode (which can either be an Ag/AgCl or saturated calomel electrode for aqueous electrolytes), and inert solid working and counter electrodes. It is good to note that a Hg/HgO reference electrode is suggested when the pH condition is alkaline, and an Ag/Ag^+ reference electrode is normally employed for non-aqueous. Inert metal wires like Au or Pt can be employed as quasi-reference electrodes. When the potential sweep method is used to evaluate the corrosion behaviour of a solid sample, the working electrode (in this instance the specimen) takes part in the electrochemical processes. Herein, the potential sweep method can either be potentiodynamic polarization or cyclic polarization. The current density obtained in the course of the examination is presented in a log scale where the active and passive states of the specimen with respect to potential are presented in the same plot. A linear scale is used to graph the potential.

Different types of voltammetry methods include linear sweep, cyclic, square wave, differential pulse, potential step, and stripping voltammetry. Linear sweep voltammetry is done by scanning the potential betwixt two set points at a needed scan rate and recording the obtained current. For the cyclic voltammetry, the potential scan is cycled between

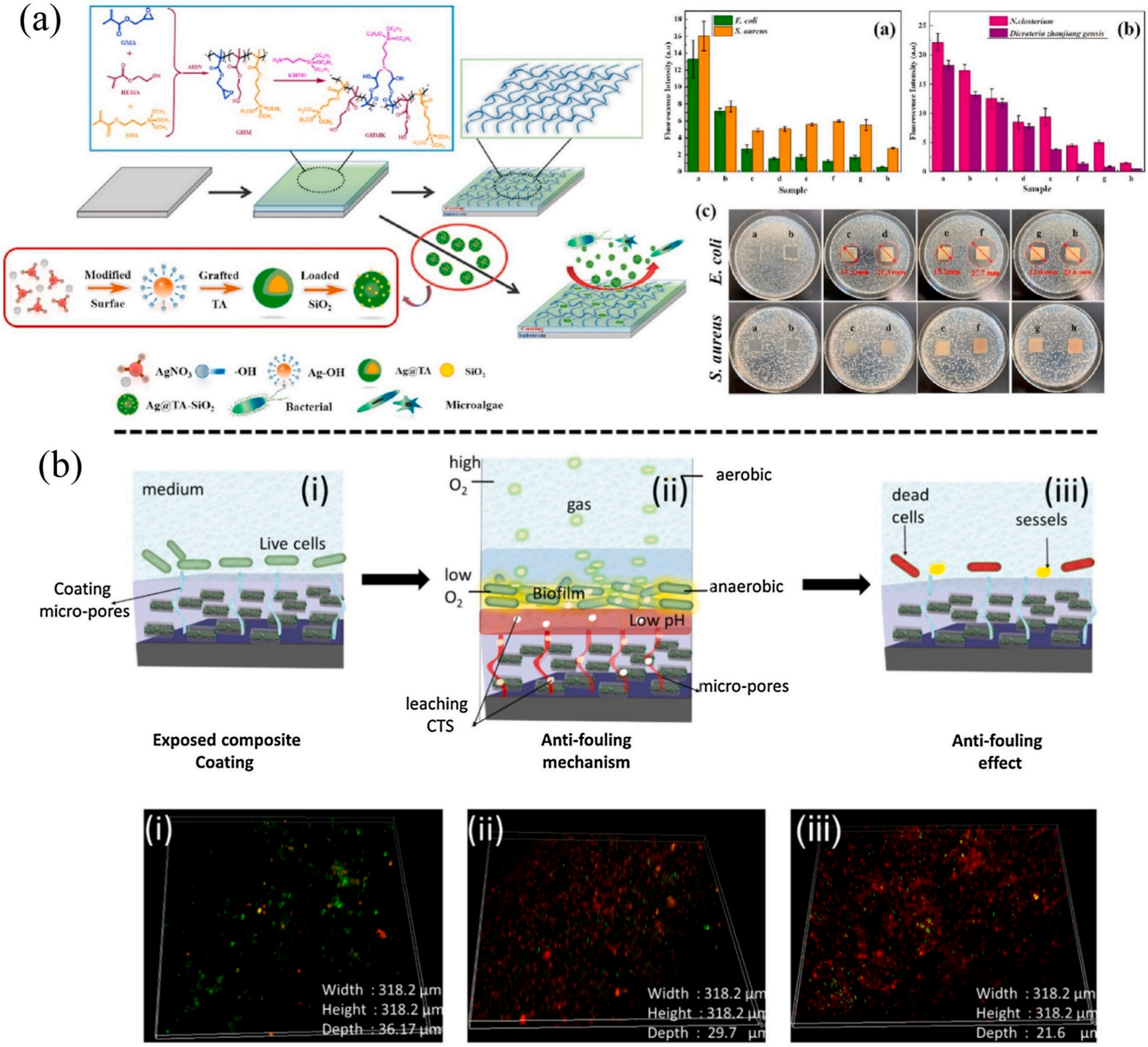

Fig. 12. Antifouling coatings achieved with nanocontainers: (a) AgNP[194] and (b) clay nanocontainers [181].

two target points as the name indicated. The potential window can cover anodic and cathodic potentials with respect to the OCP of the working electrode in the electrolytic system. Cyclic voltammetry (CV) can be applied in thin film coatings on metallic surfaces for anticorrosion applications [204] and examination of the coating performance against corrosion [205]. For instance, Siva et al. employed the cyclic-voltammetry approach to disperse a silica reservoir into an aniline oxalate solution to prepare poly(aniline-silica reservoir) coated on a steel electrode [204]. The number of cycles was shown to largely influence the formation and thickness of coating. Also, the presence of the silica reservoir during the recurrent cyclic voltammetry scans restricts the polymer oxidation process and the composite coatings had very good electroactive properties. Chen et al. added molybdate-loaded TiO_2 nanotubes into conducting polypyrrole (PPy) coatings via CV technique in order to shield 304 stainless steel from corrosion [206].

6.1.2. Tafel polarization techniques

Tafel polarization is one of the common methods used in corrosion research for examining the kinetics and processes of corrosion reactions. This technique clearly elucidates the corrosion rate, corrosion susceptibility, and behaviour of various materials in corrosive environments. The foundation for this approach is based on the Tafel equations which link the current density of the electrode to the applied potential. Hence, researchers can correctly determine the corrosion rate of a metal using the Tafel polarization technique. The polarization curve (also known as the Tafel plot) is generated by examining the current density at diverse applied potentials. The corrosion rate is calculated by the slope of this curve at the corrosion potential where a steeper slope means that there is a faster deterioration rate [212]. Darris and Shibli used the polarization technique to examine various nitrogen-based corrosion inhibitors laden mesoporous silica nanocomposites and their impact in 20% H_2SO_4 solution for regulating extended oxidation rate on steel surfaces [213]. Benzimidazole-encapsulated mesoporous silane was shown to have 99.53% inhibitory efficacy. Patra et al. used this technique to show that halloysite nanotubes with less BTA loading have better corrosion suppression (current density $= 5.3 \times 10^{-10}$ A/cm^2) compared to halloysite

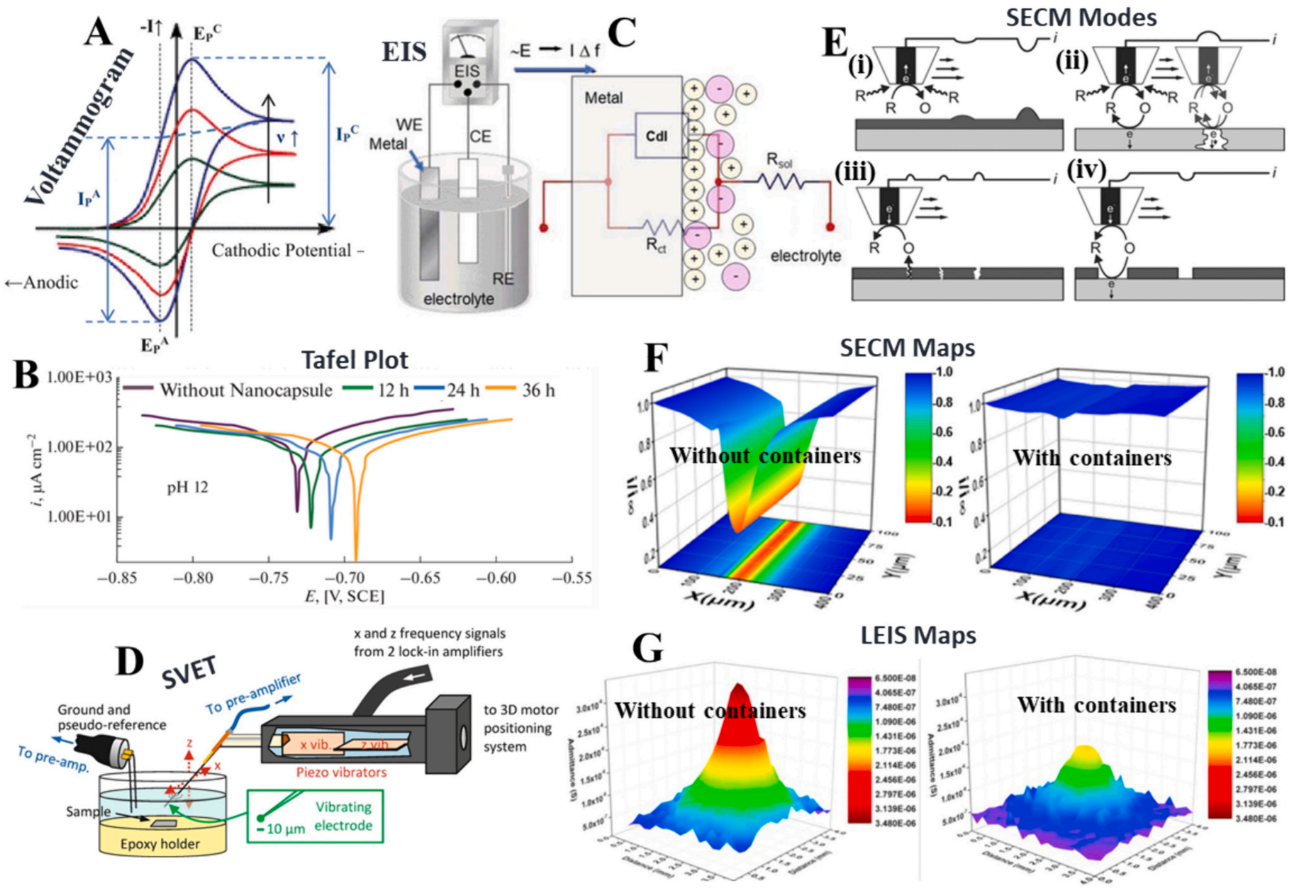

Fig. 13. (a) CV plot at varying potential scan rates (ν) [203]. (b) Tafel polarization curve of steel coated with coating laden with Hexamine inhibitors when immersed in 3.5% NaCl solution [207]. (c) Electrochemical impedance spectroscopy (EIS) set-up [208]. (d) Scanning vibrating electrode technique (SVET) set-up [209]. (e) Different modes of SECM operations for corrosion studies and their current responses respectively taken at the microelectrode; (i) Negative feedback SECM test to record the alterations in the morphology of the coatings utilizing an indirect redox mediator, (ii) Positive response measurement over a metal showing composition heterogeneities, (iii) Substrate-generation/tip-collection examination of ions/molecules obtained from a coated/uncoated metal surface, (iv) Pitting corrosion examined with the redox-competition mode [210]. (f) Scanning electrochemical microscopic (SECM) maps showing the suppression of corrosion activities in an epoxy coating doped with ethylene vinyl acetate microspheres encapsulated with $Ce(NO_3)_3$ inhibitors [211]. (g) Localized electrochemical impedance spectroscopy (LEIS) maps showing the self-healing capabilities of polydopamine (PDA) microcapsules loaded with BTA [166].

nanotubes with higher BTA loading (current density = 8.9×10^{-6} A/cm^2) after one-hour immersion in 3.5% NaCl electrolyte [214]. Fathabadi et al. used the Tafel polarization approach to prove the anticorrosion ability of intelligent pH-sensitive nanocontainers laden with Hexamine inhibitors [207] (Fig. 13b). Solutions with nanocontainers were shown to possess lower corrosion currents than solutions without the nanocontainers. On exposure to very low and high pH systems, the nanocontainers can intelligently discharge the corrosion inhibitors loaded into them and protect the steel surface with 79% efficiency.

6.1.3. Electrochemical impedance spectroscopy (EIS)

EIS is a quick, non-destructive, and highly effective tool for evaluating the corrosion processes happening on a material. It utilizes a low-amplitude AC signal to examine the distinctive impedance of the corrosion cell by scanning over a wide frequency range. Herein, it assesses the persistency of the films developed by the corrosion inhibitors and thoroughly interprets the corrosion processes happening during the film's formation and destruction. Also, it aids in predicting the corrosion protection mechanisms offered by the inhibitors. The important advantage of the EIS technique compared to other corrosion assessment approaches is that the amplitude of the potential wave is usually small (about ±10 mV), hence the system to be measured is not disturbed [152]. EIS is normally performed on Potentiostat/Galvanostat with an enhanced impedance analyzer. The electrochemical cell is made up of three electrodes system; the working electrode used for the base metal under investigation, counter electrode example platinum or stainless-steel wires, and reference electrodes which can be Ag/AgCl (Fig. 13c). During the EIS measurement, the impedance (Z), and the phase angle happening betwixt the resulting current and the applied potential (δ) are assessed with respect to the applied frequency.

Ren et al. recently used EIS technique to assess the corrosion performance of pH-responsive smart container system prepared using the metal-organic framework PCN-222 and 8-hydroxyquinoline (8-HQ) inhibitor [215]. The authors used different EIS parameters obtained from the equivalent electrical circuits (EEC) to interpret the behaviour of the coatings. For instance, the difficulty of electron transfer on the Al metal substrates was explained by evaluating the R_{ct} (charge transfer resistance) detailing the electrochemical properties of the metal/coating interface. R_c (coating resistance) was employed to examine the porosity of the coating. Zhe et al. used EIS measurements to monitor the stimuli-responsive behaviour of epoxy coating in the presence of the nanocontainers (benzotriazole (BTA) stored in mesoporous silica nanoparticles) [216]. The analysis showed that the impedance value of the BTA/epoxy coating remains nearly unchanged after 6 h of immersion in 3.5% NaCl solution strongly suggesting the protective ability of the coating. However, a significant decrease in the impedance value was observed after 24 h indicating damage to the protective adsorption film of BTA on the exposed substrate as confirmed by the reduction in R_{ct}

value.

6.1.4. Local electrochemical techniques

Electrochemical techniques such as EIS or CV are normally used to enhance the awareness of multi-phase reactions, permitting the kinetics of heterogeneous electron-transfer reactions, adsorption processes or coupled chemical reactions to be evaluated. In these traditional electrochemical measurements, the feedback of the electrode to a disturbance signal correlates to a surface-averaged assessment attributable to the conduct of the entire surface of the electrode [217]. Nevertheless, electrochemical systems hardly exhibit an ideal behaviour, and this can result in difficulties in data analysis and interpretation. For example, in situations of localized corrosion, surface-averaged methods will not be able to recognize the initiation time or the point of a distinct attack [217]. To address these challenges, various scanning methods utilizing electrodes of small dimensions (like microelectrodes) have been designed to investigate in situ the electrochemical interface. Generally, “local electrochemical techniques” is a term that includes methodologies such as scanning vibrating electrode technique (SVET) or the scanning electrochemical microscopy (SECM) or the local electrochemical impedance spectroscopy (LEIS). LEIS is specifically suited for the evaluation of complex processes happening at polarized interfaces [218].

6.1.4.1. Scanning vibrating electrode technique (SVET). SVET assesses the local electric field over a sample’s surface in a solution, permitting electrochemical actions to be visualized as they take place [219]. SVET has been extensively used in corrosion and coatings examinations because of its ability to exploit the potential gradient that exists above a typically active, or biased sample in an electrolytic solution to map its local current density [220]. SVET uses the sweep scan approach, where the probe undertakes uninterrupted measurements throughout each line. By vibrating the SVET probe, it achieves a higher signal to noise ratio. Interestingly, the information obtained from this technique is exclusive and cannot be gotten from any other method. An SVET set-up is shown in Fig. 13d [209].

Gnedenkov et al. used SVET technique to analyse the suppression of corrosion activities on MA8 magnesium alloy [221]. Prior to the test, the alloy was coated with plasma electrolytic oxidation (PEO) based coatings and further functionalized with layered double hydroxides (LDH) which worked as nano-reservoirs for the corrosion inhibitor. SVET data showed a reduction in corrosion process at the microscale, defined by the decrease of the alkaline region with low local current density inside the deliberately made two-point defect area for the samples that have corrosion inhibitors. Ren et al. used the SVET method to visually explain the suppression of the cathodic reaction occurring on the surface of an epoxy coated Al alloy due to the presence of an inhibitor loaded smart containers [215].

6.1.4.2. Scanning electrochemical microscopic (SECM) technique. SECM is a useful tool in evaluating the local electrochemical reactivity with elevated spatial and temporal resolution making it helpful for the understanding of corrosion processes and strategies for corrosion mitigation. As a tool used for scanning, SECM takes advantage of the differences in the faradaic current as the tip moves on the surface of the electrode. Enabling the tips to scan the nearby vicinity of the surface of the substrate, allows high-resolution details (from submicron to nanometer dimensions) about electrochemical activities or ion fluxes happening at the liquid–liquid and solid–liquid interface to be obtained [222]. Also, the desire to achieve steady-state currents without the usual challenges of iR drop, convection impacts, and charging current allow the ultra-microelectrode (UME) as a scanning tip to examine the whole range of electrochemical phenomenon over the surfaces [223]. In SECM technique, UME is referred to an electrode with at least one side less than 25 μm [210]. SECM can give perceptible details about the electrochemical and topographic features of a surface, though the UME influences the precision of the information [224].

SECM experiments can be carried out under varying operational modes as comprehensively depicted in Fig. 13e [210]. For instance, Feedback mode offers many advantages in examining the corrosion of material. This is because, besides quantifying the basic developments in reactivity of the immersed sample, it is also perceptive to slight alterations in the topography of the substrate [210]. The Generation/Collection (GC) modes are commonly applied in the evaluation of corrosion properties because of their capacity to monitor a direct mediator. Generally, when a metal is immersed, it undergoes dissolution to produce ions/molecules that can be amassed at a nearby microelectrode. So, the flux of ions or molecules can be examined upon sample immersion to explain the local corrosion rates [225]. A subgroup of the GC modes known as Anodic Stripping Voltammetry (ASV) can be used to examine ions that are reduced at very low potential (such as zinc) [226]. Also, Potentiometric mode has been used to gain local insights into the generation of certain ions such as Zn^{2+} generated at the metal surface [227]. Ma et al. employed the redox competition mode to explain the suppression of corrosion activity in an epoxy coating containing mesoporous SiO_2 loaded with benzotriazole and 2-mercaptobenzothiazole inhibitors [228]. From a local electrochemistry viewpoint, the SECM results showed a significant increase in the oxygen reduction currents due to the slow discharge and adsorption of inhibitors that limited the cathodic corrosion activity on the Al alloy. Similarly, Ren et al. [211] and Wang et al. [229] both applied the redox competition mode to show the suppression of corrosion activities in an epoxy coating containing inhibitor loaded microcontainers as seen in Fig. 13f.

6.1.4.3. Localized electrochemical impedance spectroscopy (LEIS). Isaac and co-workers proposed a novel technique for obtaining quantitative local electrochemical impedance spectroscopy [230,231]. The fundamental of this approach is established on the theory that the local impedance can be obtained by measurement of the ac-local-current density in the neighbourhood of the working electrode in a normal three-electrode cell system [231]. This was obtained by the application of a dual microelectrode for detecting the local ac-potential gradient, the local current being gotten from the direct employment of the Ohm’s law. Also, 10 μm diameter platinum microelectrodes positioned 170 μm aside was shown to permit 30 - 40 μm resolution, which favourably correlated with the SVET determined results [217]. Till date, the best spatial resolution of the LEIS method is about 10 μm. However, this resolution can be enhanced by reducing the dimension of the probe and the separation distance between the microelectrodes. Also, by utilizing an electronic device to annul the DC offset between them. The latter will permit a larger amplification gain to be employed and thus working in concentrated solution with small electrode size [218].

Liu et al. applied the LEIS technique to show that the anticorrosion capacity of a scratched coatings can be restored [232]. The coating was mixed with graphene/β-cyclodextrin-based supramolecular nanoreservoir loaded with BTA inhibitor. Cheng et al. used LEIS to confirm the corrosion suppression and self-healing properties of polydopamine (PDA) microcapsules loaded with BTA as observed in Fig. 13g [166].

6.1.4.4. Scanning kelvin probe (SKP) technique. Rohwerder and co-workers have utilized the scanning kelvin probe (SKP) technique in driving an understanding of the diffusion kinetics of corrosion inhibitors or delamination of coatings in the presence of nano/microcontainers [233–235]. This is potentially useful for researching the leakage of corrosion inhibitors from nano/microcontainers in anticorrosive coatings. A typical example of potential profiles obtained from a cathodic delamination study using SKP is shown in Fig. 14 [234]. When silica concentration rises, the delamination rate falls, and for silica additions more than 0.5%, the delamination process shifts from a sqrt(t) time dependence to a linear time dependence. The intact area has a potential in the range of 0 - 0.2 V_{SHE}. The potential under the delaminated area

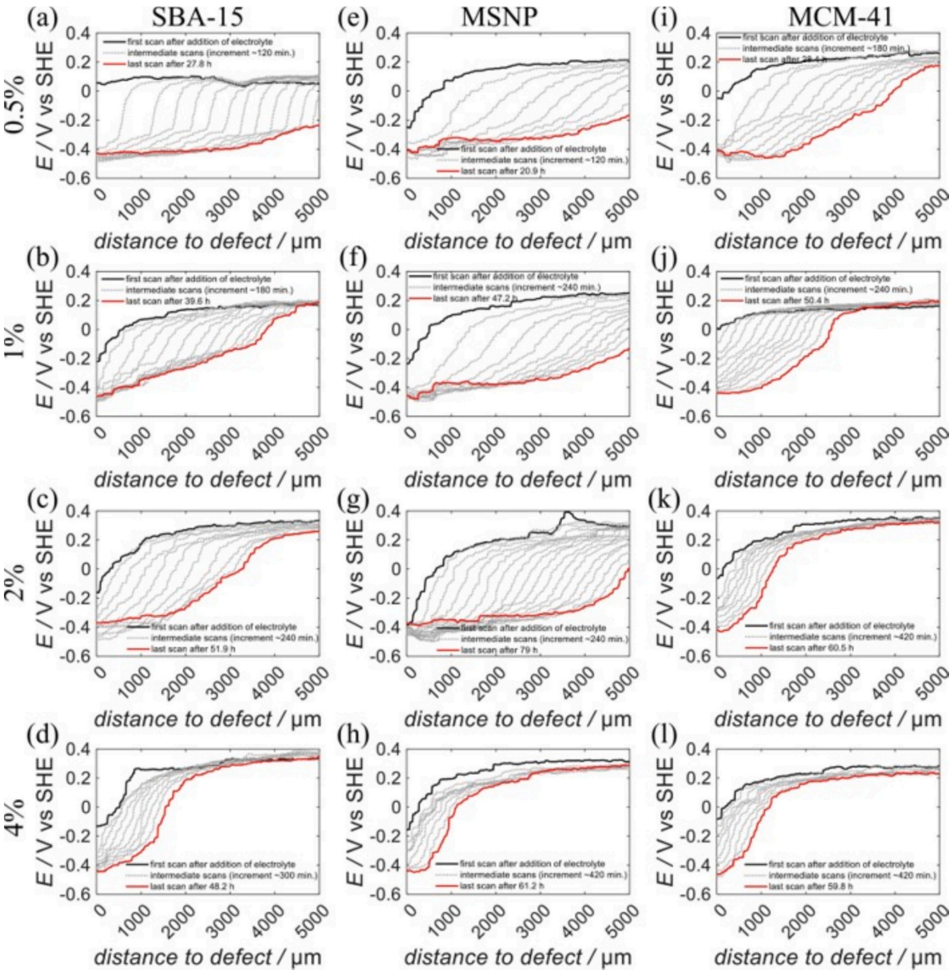

Fig. 14. Potential profiles obtained using SKP for cathodic delamination of PVB coatings doped with SBA-15, MSNP, and MCM-41 mesoporous silica particles on Fe substrate [234].

changes towards the defect potential, approximately -0.4 V_{SHE}, when the coating begins to delaminate from the defect site into the intact coating. The findings demonstrate that the delamination rate on Fe can be effectively reduced by adding mesoporous silica to the PVB coating. The degree of cathodic delamination rate inhibition appears to be influenced by the size of mesoporous SiO_2. When Fe is used as the substrate, it is found that the rate of cathodic delamination decreases more sharply as the size of the mesoporous SiO_2 particles in the PVB coating increases. The coating with the lowest cathodic delamination and the best corrosion resistance is the one containing 4% MCM-41.

6.2. *Photospectroscopy technique*

Photospectroscopic methods are normally applied together with other electrochemical techniques to investigate corrosion activities such as dissolution, passivation and inhibition occurring in specimen. They can either be applied in-situ or ex-situ to examine the surface of the material or corrosion products. These methods include photo absorption spectroscopy (utilizing infrared and ultraviolet–visible (UV–Vis) light sources), and vibrational spectroscopy like Fourier Transformed Infrared (FTIR) spectroscopy and Raman Spectroscopy.

6.2.1. *Application of UV-vis spectroscopy in anticorrosive coatings with nano/microcontainers*

In the area of porous nano/microcontainers application, UV–vis spectroscopy is mostly employed to show the discharge of inhibitors from the containers in different pH media. However, they have been proven effective in the detection of early corrosion [236]. Early corrosion detection can permit workers to either mend or change the affected coatings in time thereby prolonging their service life and minimizing the chances of corrosion failure. For example, Liu et al. reported the fabrication of a self-sensing and active anticorrosion coating using pH-responsive multiple layer chitosan/alginate-wrapped $CaCO_3$ microcontainers laden with 1,10-phenanthrolin-5-amine (APhen) [237]. The containers were shown to react to the variations in pH to releasing APhen which works as both a corrosion guage and an inhibitor. The authors presented UV–vis spectra of 1 mM APhen aqueous solutions with the inclusion of varying amounts of $FeCl_2$ under various pH environments. A fine band at 520 nm was shown relating to the development of a Fe^{2+}-APhen complex ($[Fe(APhen)_3]^{2+}$). Therefore, the APhen molecules work as an active sensor to monitor the origination of Fe^{2+} ions from initial corrosion of metal. In another experiment involving HNTs laden with 8-hydroxyquinoline (8HQ) with the shell composed of sodium tripolyphosphate-chitosan (CS) mixed into epoxy matrix, the researchers utilized UV–vis spectroscopy to show that the formation of 8HQ-Fe can indicate early corrosion detection when a coated steel is put into in 3.5% NaCl solution [238].

6.2.2. *Application of FTIR spectroscopy in anticorrosive coatings with nano/microcontainers*

Infrared spectroscopy depends on the reciprocal action between IR radiation and molecules that leads to the intake of IR radiation by the molecules. At temperatures beyond absolute zero, all the atoms in molecules are in steady vibration in relation to one another. When the frequency of a distinct vibration is commensurate with the frequency of the incident IR radiation, the molecules absorb the radiation. The absorbed radiation meets the transition energy of the bond or group that vibrates in the molecule. Tong et al. recently used FTIR technique to confirm the self-healing effect of an organic coating made using ZIF-8-capped $CaCO_3$ microcontainers having tung oil healing agent and 1,10-phenanthrolin-5-amine (APhen) corrosion indicator/inhibitor [239]. The FTIR intensity mapping showed a strong presence of tung oil at the scratch region after 7 days in 3.5% NaCl solution. The FTIR spectra confirmed the peak indicating unsaturated C=C bonds during the curing of tung oil at the scratch site and the presence of APhen. FTIR spectra was used to show the inhibitive ability of SiO_2 nanocontainers containing BTA after the coated sample was immersed in 3.5% NaCl for 30 days [240]. The peak seen at 1209 cm^{-1} in the spectra is attributable to the S-N=N-N- breathing vibration which comes from the BTA inhibitors only.

6.2.3. *Application of Raman spectroscopy in anticorrosive coatings with nano/microcontainers*

Raman spectroscopy is a non-destructive approach which depends on the effect of inelastic light scattering by molecules. It provides fingerprints for molecules which can be used in identification and description. This technique was used to prove the self-healing ability of tung oil when an epoxy coated sample with nanocontainers laden with tung oil was immersed for 70 days in a corrosive environment [239]. Wang et al. employ the Raman technique to analyse the corrosion products after a coated steel sample was exposed to corrosive environment [236]. The coating was based on UF microcapsules containing 1,10-phenanthroline (Phen) molecules. The Raman spectra confirmed the adsorption of Phen on the substrate. Liu et al. used this approach to confirm the generation of Fe^{2+}-APhen complex on coated Q235 steel after 24 h in 3.5 % NaCl solution [237]. The coating was based on $CaCO_3$ micro-reservoirs containing 1,10-phenanthrolin-5-amine (APhen). Ding et al. used the Raman technique to detect organic corrosion inhibitor 8HQ at the scratch site of Mg alloy exposed to corrosive media [241]. The alloy was coated with a coating containing smart nanocontainers that are prepared based on the build-up of supramolecular assemblies (bipyridinium $\subset$ water-soluble pillar[5]arenes) atop the exterior surface of magnetic nanovehicles (Fe_3O_4@mSiO_2), connected by disulfide linkers. The supramolecular assemblies with high binding affinity as blockers for the loaded 8HQ. This detection confirmed that the coating system provided a quick response time and fast self-healing.

6.3. *Microscopy techniques*

Microscopy techniques are non-destructive approaches developed to examine corrosion occurrence and corrosion rates via the observation of the surfaces of the corroded samples. The images show the surface topography, roughness, cracks, pits, and other interesting appearances of the corroded samples. Table 3 is the list of different microscopic techniques and their applications.

Table 3
List of different microscopic techniques.

Technique	Application	Reference
Optical microscopy	Rapid observation of the 2D images of the surface.	[237,238]
Atomic force microscopy (AFM)	2D and 3D images are visualized at high resolution. Also gives the surface roughness parameters and can be used for in-situ observation of the corrosion processes.	[242]
Scanning electron microscopy (SEM)	Surface image visualization at very high magnification.	[243,244]
Transmission electron microscopy (TEM)	Surface image visualization at nanoscale resolution. Very thin samples are needed for observation. In situ TEM can be carried out for corrosion studies	[245]

7. Desirable properties, current challenges and prospects of anticorrosive coatings doped with nano/microcontainers

Organic coatings remain the most widely applied method for protecting metallic materials against corrosion. The incorporation of nano/microcontainers in coatings has paved the way for a wide ranging and exciting field of research for obtaining coatings with better performance in service, durability, and tailor-made features. While they are expected to have impressive anticorrosive properties, they must also be continuously updated with more environmentally friendly functionalities to ensure their relevance to current sustainable technologies [246].

Figure 15 depicts the array of desirable properties organic coatings should possess, which highlights their multifunctionality so that they can respond to changes in the environment. In addition, these coatings must be able to sense corrosion before it eats deep, heal coating defects, be anti-fouling and prevent additional corrosion better than the conventional corrosion-resistant coatings [247,248].

The use of these organic coatings on metallic surfaces ensures that the rate of corrosion is systematically reduced because organic coatings form a barrier protection against the diffusion of oxygen onto the metal surface. However, in some cases, the barrier-forming property of the organic coating fails to prevent the diffusion of water and oxygen molecules leading to unlimited corrosion attack [249].

Resulting from their outstanding mechanical properties, excellent adhesion capacity to metal surfaces, great resistance to chemical attack and wide availability at low prices, organic coatings, such as epoxy (EP) are popular materials employed for preventing the transport of corrosive ions to the surfaces of metallic substrates. However, they are prone to the formation of microspores during evaporation, thereby leaving pathways for corrosive ions to reach the protected surfaces over time. This drawback has encouraged the application of several interventions towards improving the shielding effect of organic coatings, popular among the many methods are the use of fillers, which is considered a cost-effective option. Researchers have used a wide array of materials for this purpose [250–253]. However, most of these materials are poorly compatible with the matrixes of the organic polymers, leaving filler agglomeration within the polymer mix, resultantly minimizing the shielding effect of the coatings. Based on this, recent studies have tilted towards the use of materials that contain reactive functional groups that can bind with the polymers to promote their even dispersion within the polymer matrixes. Duan et al. applied zeolitic imidazolate framework-8 (ZIF-8), a well-known metal organic framework as a nanofiller for EP, and the modified EP exhibited enhancements in both its cross-linking property and corrosion protection ability. The enhanced cross-linking was attributed to the ease of reactivity between EP and the amine groups in ZIF-8 which permitted an agglomeration-free formulation. This consequently improved the mechanical property of EP and endowed it with better protectability [254]. Similarly, zeolitic imidazolate framework-12 (ZIF-12) was employed in EP fabrication by Abdolmaleki et al. in a comparable situation, and in addition to the improved mechanical properties, increased cross-linking density and excellent anticorrosion performance of the resulting EP coating, the modification afforded significantly improved glass transition temperature and EP coating break energy [255]. Other specific fabricated nanoporous materials in the literature for complementary corrosion protection applications are silica/2D-covalent organic framework nanocomposites [256] and some graphene-based formulations [257–260].

Even though the design of coatings is still being developed to meet other desirable properties, there are several challenges posed especially when using the conventional anticorrosion coating. These include the scalability of production, cost-effectiveness, and ensuring long-term stability. Thus, the traditional anticorrosive coatings with limited functions can no longer meet the prevailing requirements.

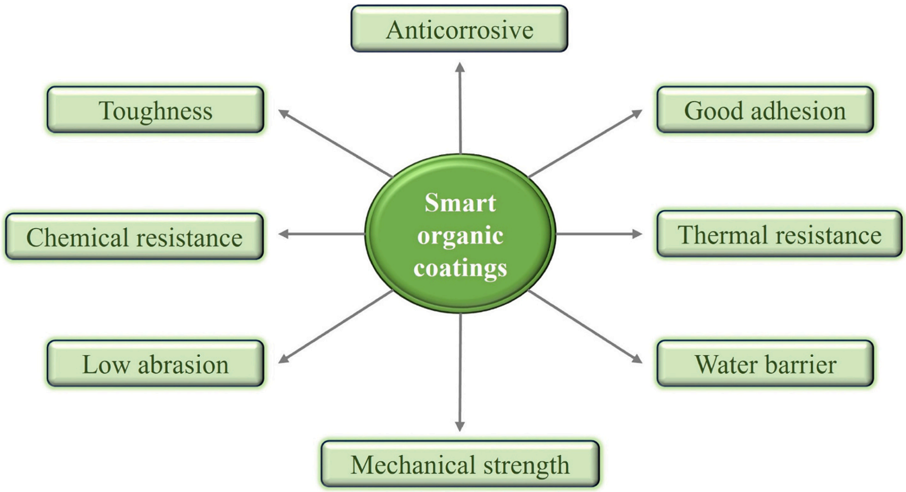

Fig. 15. Desirable properties of organic coatings for a wide range of applications.

Meanwhile, the most recent advances in the incorporation of nano/microcontainers in coatings have paved way for new opportunities and gains in integrating multifunctionality. In effect, robust designs which incorporate smart functionalities are particularly promising. Such models confer nanocomposites tunable properties which can be harnessed to obtain coatings with minimal human intervention during maintenance yet provide robust protection to metals.

8. Conclusion

The incorporation of nano/microcontainers in organic coatings for anticorrosive application is reviewed in-depth in this work. These containers offer enhanced corrosion prevention and resistance. Incorporation of nanomaterials into polymeric coatings can significantly improve their barrier performance by decreasing porosity and altering the diffusion path for corrosive species such as oxygen and chloride anions. Their ability to respond to environmental changes has been harnessed to develop smart responsive coatings whose properties can be tuned to obtain multifunctionalities. The encapsulation of inhibitors and/or healing agents with nano/microcontainers doped into the coatings in an appropriate manner is essential for extending their shelf life and improving the responsiveness of these coatings. For use in anti-corrosion coating applications, the containers must be compatible with standard coating resins and their fabrication process must be economical. Importantly, the more sophisticated self-healing coating of the future is expected to restore more intricate and macroscopic damage as well as the mechanical and functional characteristics of the coatings. This comprehensive review sheds light on cutting-edge technologies and mechanisms of action for nano/microcontainer based anticorrosion coatings.

CRediT authorship contribution statement

Inime I. Udoh: Writing – review & editing, Writing – original draft, Formal analysis, Conceptualization. **Okpo O. Ekerenam:** Writing – review & editing, Writing – original draft. **Enobong F. Daniel:** Writing – review & editing, Writing – original draft. **Alexander I. Ikeuba:** Writing – review & editing, Writing – original draft, Conceptualization. **Demian I. Njoku:** Writing – review & editing, Writing – original draft, Conceptualization. **Sharafadeen K. Kolawole:** Writing – review & editing, Writing – original draft, Conceptualization. **Ini-Ibehe N. Etim:** Writing – review & editing, Writing – original draft. **Wilfred Emori:** Writing – review & editing, Writing – original draft. **Chigoziri N. Njoku:** Writing – review & editing, Writing – original draft, Conceptualization. **Iniobong P. Etim:** Writing – review & editing, Writing – original draft. **Paul C. Uzoma:** Writing – review & editing, Writing – original draft.

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

The authors do not have permission to share data.

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