

# Corrosion inhibitor—loaded smart nanocontainers

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## 1. Introduction

Traditional approaches for preventing and controlling corrosion of metal-framed structures include several methods: (1) electrochemistry (cathodic protection and anodic passivation), (2) barrier coating protection, and (3) metallurgical design [1]. Practice has shown that the most effective results are obtained when two or more of these strategies are combined. However, neither of them provides an ideal solution, as they have limited effects on corrosion protection and are often associated with high production costs and the use of materials that have adverse effects on human health and environment. As an example, hexavalent chromates ( $\text{Cr}^{6+}$ ), an oxidizing oxyanion of chromium, has been among the most used inhibitors for corrosion protection over 100 years as they are efficient in forming protective oxide layers at damage sites [2]. The carcinogenic and toxic nature of chromates, however, has caused them to be banned recently by the European Union directive of the Registration, Evaluation, Authorization and restriction of Chemicals (REACH) [3,4]. To date, the use of chromates has been stopped in almost all main industries. Thus, increased efforts are invested to find environmentally and health benevolent substitutes. In order to employ reliable alternatives to chromates, anticorrosion coatings should comply with all the regulations, reduce the production and maintenance costs, and assure at least equivalent or even better performance. The development of competitive corrosion inhibitor systems must consider the solubility of the inhibitor, the compatibility between the carrier and inhibitor, the compatibility between carrier and the coating system, as well as the water permeability of the protective coatings.

The idea to incorporate encapsulated active anticorrosion agents in various materials and coatings was first proposed in the early 1990s [5,6]. A decade later, White et al. [7] elaborated further this idea in order to create corrosion-protective composite coatings. As many

following studies in this field show, the use of smart nanocontainers as carriers of corrosion inhibitors offers good alternatives to classical corrosion protection methods. The presence of smart nanocontainers in protective coatings provides anticorrosion properties either through a stimulated response to changes in the external environment or as an autonomic response to fluctuations in the coating integrity. Nanocontainers can be defined as nanosized hollow and/or porous structures that contain the active substances in its interior (hollow) or in inner cavities (porous) [8]. Some typical structures used as the carriers of the corrosion inhibitors are micelles, vesicles, dendrimers, nanocapsules, nanotubes, and nanolayers [9]. Scanning electron microscopy (SEM) images of some typical nanostructures used as corrosion inhibitor nanocontainers are presented in Fig. 12.1.

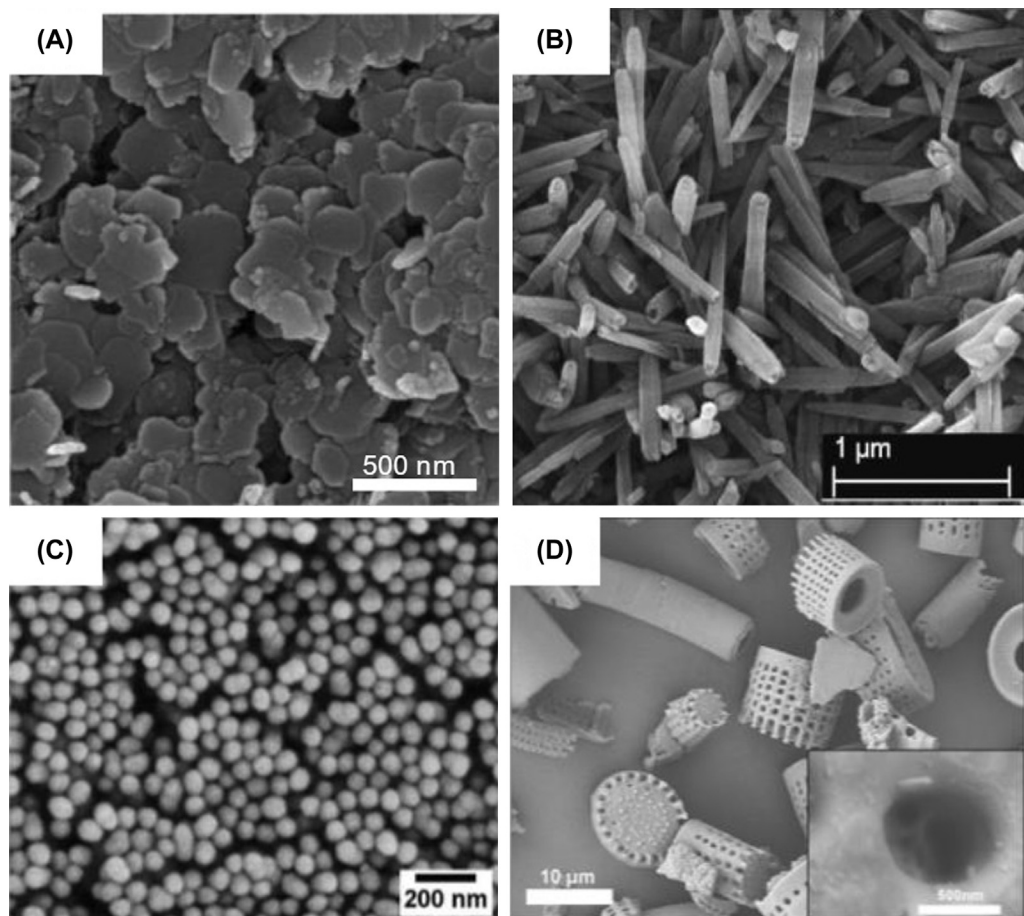


FIGURE 12.1 SEM images of some typical nanostructures used as corrosion inhibitor nanocontainers: (A) layered double hydroxides, (B) halloysite, (C) mesoporous  $\text{SiO}_2$ , and (D) diatomaceous earth. Reprinted with permission from F. Zhang, P. Ju, M. Pan, D. Zhang, Y. Huang, G. Li, X. Li, *Self-healing mechanisms in smart protective coatings: a review*, *Corros. Sci.* 144 (2018) 74–88. <https://doi.org/10.1016/j.corsci.2018.08.005> and <http://creativecommons.org/licenses/by/4.0/>.

The incorporation of corrosion inhibitors into smart nanocontainers can be achieved by employing several different approaches: (1) physical absorption of the inhibitor through the porous nanocontainer structure, (2) various encapsulation processes, (3) ion exchange reactions with the available counterions in the respective nanocontainer, and (4) embedding of the inhibitor between alternating polyelectrolyte (PE) multilayers [11].

At the present time, the development of nanocontainers used in corrosion protection coatings has reached a level where major efforts are focused now on the upscaling of nanocontainer production while testing the systems in industrially relevant environments [12]. Furthermore, the knowledge gained while developing systems for anticorrosion purposes inspired other branches of material science to extend development and potential application of smart nanocontainers in the areas such as biomedicine, energy storage, antibacterial, and antifouling applications, to name a few.

This chapter aims to give a concise review on various types of nanocontainers for corrosion protection coatings, their fabrication methods, as well as explanation of the different corrosion inhibition mechanisms. Research results of improved corrosion resistance by introduction of smart nanocontainers into coatings are summarized. The commercial viability of those innovative materials and processes is discussed and evaluated in the chapter.

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## 2. Nanocapsules

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### 2.1 General aspects of corrosion inhibition with nanocapsules

Nanocapsules loaded with corrosion inhibitors possess several advantages over traditional corrosion protection coatings. In response to different stimuli such as mechanical, electrochemical (e.g., changes in electrochemical potential), or chemical attack of the protective coating, nanocapsules near the damage site are affected. Consequently, entrapped inhibitor is released locally for the termination of further destructive processes. Therefore, corrosion inhibition is achieved, which is targeted, timely and only on demand. Additionally, the use of nanocapsules as an active substance carrier retains the inhibitor's effectiveness over time, in cases where adverse reactions between the inhibitor and the coating are expected [13,14]. However, the challenge related to this approach is to achieve uniformity of the nanocontainer distribution in the protective coating. The dispersion methods used for fabrication and the resulting dispersed (embedded) amount of the capsules in the protective coating are very important because they affect directly the rheological and mechanical properties of the corresponding composites [15]. Additional important challenge is to overcome the limited repeatability of the corrosion inhibition process itself. Once corrosion inhibitor is released it cannot be reused, and therefore, those sites remain potentially unprotected in the event of renewed attacks.

### 2.2 Fabrication methods for nanocapsules

There are several different methods that enable the successful fabrication of nanocapsules containing corrosion inhibitor: layer-by-layer (LbL) deposition, direct encapsulation, and in situ emulsion polymerization [16–19]. In the LbL assembly technique, alteration of the

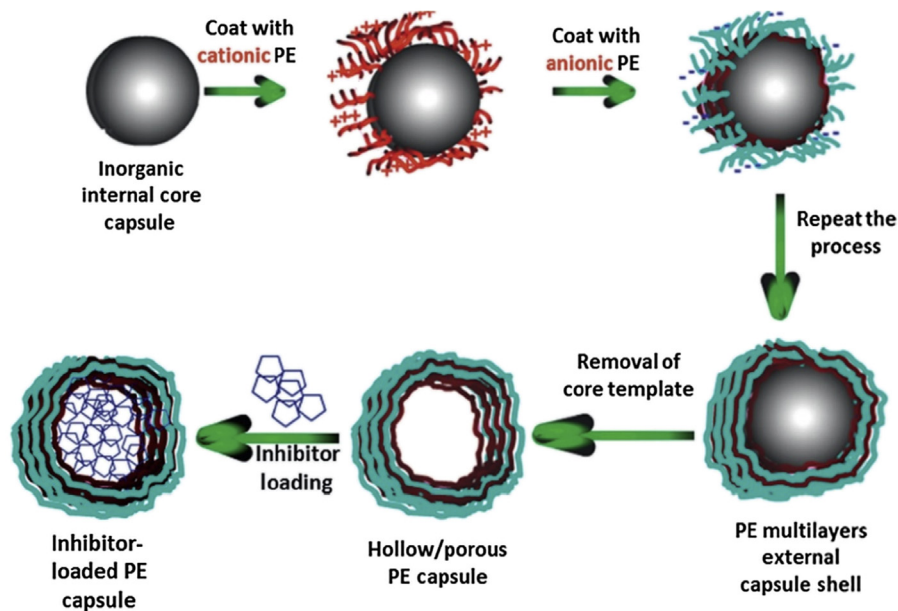


FIGURE 12.2 Schematic illustration for the preparation of polyelectrolyte (PE) capsules using template inorganic core methodology. Reprinted from A.S.H. Makhoul, D. Scharnweber, *Handbook of Nanoceramic and Nanocomposite Coatings and Materials*, first ed., Elsevier, 2015 (Chapter 24), with permission from Elsevier.

surface charge permits continuous fabrication of the layered structure. The key feature of this technique is the precision provided to control the thickness of nanocapsule shell and therefore the size of nanocontainer. Molecular species of opposite charge are adsorbed alternately to the surface, either planar or colloidal, resulting in the formation of a nanoscaled thin film [20], as described in Fig. 12.2. The process is continued until the desired number of layers, i.e., capsule shell thickness is achieved. However, the driving force for the LbL assembly is not necessarily limited to electrostatic interaction. Other interactions such as hydrogen bonding and metal coordination can be used for the assembly as well [21]. For fabrication of nanocapsules containing corrosion inhibitor, the active agent is encapsulated between oppositely charged PE layers [22]. This method provides a good bonding of organic functional groups to the metal surface and good barrier properties for corrosion protection.

Ceramic, hollow, or mesoporous nanoparticles can be used as a scaffold (i.e., container core) alone, or in combination with the LbL fabrication technique. Thus, ceramic nanoparticles can act as spongelike reservoirs that can be loaded with corrosion inhibitors [23]. For this purpose, naturally occurring or otherwise synthesized ceramic nanoparticles are mixed with the concentrated solution of the inhibitor in an appropriate solvent (or with pure inhibitor, in the case of liquid inhibitors). In addition to the good wetting ability of the proper solvent and excellent solubility of the chosen inhibitor, porosity and pore (cavity) size distribution of the ceramic particles play an essential role in the loading capacity. LbL-assembled PE shell serves to restrain an adverse leakage of the corrosion inhibitor from the nanocontainer core.

Starting point for the preparation of all specific types of emulsion-based containers is the creation of so-called “direct” oil-in-water (O/W) or “inverse” water-in-oil (W/O) emulsion. The emulsion-based fabrication methods demonstrate several advantages over the above-mentioned methods involving LbL assembly approach. The dual role of emulsion droplets—as templates and as container cores—allows significant reduction of production steps required for assembly of nanocontainers. Moreover, the liquid state of the container cores enables the precise control of the concentrations of all ingredients. Regarding the nature (physical or chemical) of the process utilized for the formation of the nanocontainer, two main techniques are recognized. In one technique, the shell forming material begins to precipitate at the interface of the emulsion droplets containing corrosion inhibitor, which function as a soft template. Interfacial precipitation can be induced either by evaporation of the solvent of the dispersed phase, or by dilution of the dispersed phase by a nonsolvent. Another emulsion-based approach relies on the physical nature of the event. The formation of the shell is based on the phenomenon that partially hydrophobic/hydrophilic particles form spontaneously a tight mono- or multilayer at the emulsion droplets interface.

Nanocontainers obtained by in situ emulsion polymerization are formed within the course of a chemical reaction taking place in the bulk of the emulsion droplets. Realization of this technique presumes that all reactants needed for the synthesis are already from the beginning contained in the emulsion droplets [23]. After the O/W or W/O emulsion is prepared, the chemical (e.g., catalyst) or physical (e.g., UV light, temperature, etc.) triggers are activated, in order to switch on the reaction that will run until the completion of the polymerization reaction.

In some cases, the combination of several emulsion-based techniques leads to better results than the application of each of these methods alone [24].

### 2.3 Examples of self-healing coatings based on nanocapsules for corrosion protection

In this section, some selected contributions to the development of new self-healing coatings based on corrosion inhibitor-containing nanocapsules are presented.

The initiation of the corrosion activity is accompanied by local changes of pH in anodic and cathodic sites. Therefore, the most studies for controlled release of corrosion inhibitor are focusing on local change of pH as the trigger. In several studies reported by Zheludkevich and Shchukin [16,17,25], inorganic nanocarriers based on SiO<sub>2</sub> were coated with PE shells using LbL technique. The negatively charged SiO<sub>2</sub> nanoparticles were first coated with a layer of positively charged poly(ethylene imine), followed by adsorption of negatively charged poly(styrene sulfonate) (PSS) and then positively charged benzotriazole (BTA) as corrosion inhibitor. The optimum number of PSS/BTA layers was found to be two. The protection properties of the nanocapsule-embedding composite were investigated by electrochemical impedance spectroscopy (EIS) and by the scanning vibrating electrode techniques (SVETs). The self-healing composite completely prevented corrosion, owing to the released inhibitor. Just recently, Wang et al. [26] reported a method for fabricating triple-stimuli-responsive (acid/alkali/corrosion potential) smart nanocapsules loaded with BTA, by installing specially structured bistable pseudorotaxanes as supramolecular nanovalves onto orifices of mesoporous silica

nanoparticles. It was shown that the smart nanocontainers can simultaneously respond to acid stimulus at microanodic regions, alkali stimulus at microcathodic regions and corrosion potential of AA2024 around corrosive regions and quickly give a feedback to release corrosion inhibitors, forming protective molecular films on bare metallic substrates.

The “green” corrosion inhibitors, derived from plants can be considered as a renewable, nontoxic, biodegradable, cheap, and effective substitute to the synthetic corrosion inhibitors. In the recent work of Haddadi et al. [27], some remarkable active corrosion protection properties were demonstrated using walnut green shell extract as the inhibitor encapsulated in mesoporous carbon nanospheres (MCNSs). Mesoporous silica templating method was used to synthesize MCNSs. Corrosion resistance of the mild steel samples in the 3.5 wt.% NaCl solution in the presence and absence of walnut extract was compared. It was shown that the charge transfer resistance of the bare steel sample enhanced from  $\sim 610$  to  $\sim 4060 \Omega\text{cm}^2$  in the presence of walnut extract after 24 h immersion time.

Plawecka et al. [18] employed direct encapsulation method to produce nanocapsules loaded with 2-mercaptobenzothiazole (MBT). Localized EIS (LEIS) and SVET analysis revealed that the corrosion process was efficiently inhibited for AA5083 samples protected with 100-nm-size inhibitor-loaded nanocapsules incorporated in water-based epoxy coatings. When exposed to the salt spray test, the samples did not show signs of corrosion activity over 1000 h of exposure. All the as-prepared samples revealed good adhesion behavior.

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### 3. Core–Shell nanofibers and nanotubes

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#### 3.1 General aspects of corrosion inhibition with core–shell nanofibers and nanotubes

Core–shell nanofibers to be used as carriers of corrosion inhibitors are nanofibers which consist of a polymer shell and the core consisting of a corrosion inhibitor. When the core–shell nanofiber is damaged by cutting or scratching of the protective coating, the self-healing process is set into action. The core of the nanofibers is exposed, and corrosion inhibitor is released. The advantages of the use of core–shell nanofibers for self-healing and for corrosion prevention are that a good and uniform distribution of the core–shell nanofibers in the coating matrix is achievable. A uniform distribution and the nanodimensions of the fibers provide the possibility to assemble thin coatings with a smooth surface appearance and has a positive effect on coating mechanical properties. Additional advantage of nanofiber usage in a coating is that nanofibers can be produced by a relatively simple process, e.g., by electrospinning or by solution blowing, and that these production processes have already been upscaled to an industrial level.

A further advantage of using fibers with nanodimension in a coating applied for corrosion prevention is the observation that nanofibers seem to enhance the diffusion of corrosion inhibitors within the coating and thereby support corrosion inhibition and self-healing effects by its presence alone. This effect seems to be independent of the way the corrosion inhibitor is introduced into the coating either by mixing it with the coating matrix directly or by introducing it with the nanofibers itself, or in combination with the nanofibers. Such an



accelerated self-healing effect has been shown for a coating based on epoxy containing 2% corrosion inhibitor and with 0.5% cellulose nanofibers on steel in Ref. [28]. The nanofibers seem to serve as a pathway for the release of the corrosion inhibitor. When single component electrospun nanofibers of Nylon 6-6 loaded with 20% corrosion inhibitor BTA are distributed in an alkyd coating on Cu substrates, a better and more uniform distribution and dispersion of such inhibitors into the protective polymer matrix [29] is obtained. The composite layer showed improved corrosion resistance up to 500 h when immersed in a chloride ammonium sulfate solution. Polyvinyl alcohol (PVA) electrospun nanofiber mats loaded with a cerium chloride corrosion inhibitor were prepared and embedded in epoxy coatings on AA2024-T3 aluminum substrate [30].

Compared to a direct incorporation of the corrosion inhibitor into the epoxy coating, an improved corrosion protection was achieved by loading the corrosion inhibitor into the epoxy matrix via the electrospun nanofibers. A disadvantage of the use of core–shell nanofibers for corrosion prevention and for self-healing may be that the volume of corrosion inhibitor is limited due to the small core volumes of the core–shell nanofibers.

In addition to the polymer-based core–shell nanostructures, inorganic nanocontainers such as halloysite nanotubes are also recognized as economically viable and promising corrosion inhibitor carriers [31]. Halloysite with the empirical formula  $(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O})$  is a clay mineral (two-layered aluminosilicate) with predominantly hollow tubular structure, that can be mined from deposits as a raw mineral and subsequently used after purification for inhibitor loading. Depending on the deposit, length of tubules varies from 500 to 1000 nm, with inner diameter from 10 to 150 nm. The typical specific surface area of halloysite is  $65 \text{ m}^2/\text{g}$ , pore volume is  $1.3 \text{ mL/g}$ , and specific gravity is  $2.53 \text{ g/cm}^3$  [31]. According to the Price et al. [32], selective etching of the alumina layer inside halloysite lumen with sulfuric acid can provide loading capacity for corrosion inhibitors up to 60 wt.%, that is comparable with the loading capacity of polymer-based nanocontainers (40–60 wt.%) [33]. However, halloysite nanotubes treated with sulfuric acid suffer from a slight decrease in mechanical strength. Additional drawback of halloysite is the tendency to aggregate in the protective coating. Therefore, embedding of the inhibitor-loaded halloysites with the coating formulation requires intensive mixing using high-speed stirrers or ultrasound.

Recently, attapulgite (ATP), with a theoretical formula of  $(\text{Al}_2\text{Mg}_2)\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$ , a cheap and ubiquitous natural clay with fibrous structure, was introduced as an alternative for halloysite nanocontainers [34]. Typical length of ATP fibers ranges from 0.8 to 1  $\mu\text{m}$ , with 20 nm in diameter.

### 3.2 Fabrication methods for core–shell nanofibers

The electrospinning process can easily be set up in any laboratory with little investment effort. The few components required are a syringe, a high voltage supply, and a pump for delivering the polymer dissolved in a suitable solvent to the tip of the needle of the syringe. Due to the applied voltage between the tip of the syringe and a metal plate serving as a collector, a so-called Taylor cone is developing at the tip of the needle which ejects a high-speed liquid stream of dissolved polymer. The solvent is evaporating quickly in air leaving a polymer nanofiber, which is deposited onto the collector. A variation of this simple arrangement

can be used to produce core-shell nanofibers. Coaxial electrospinning or coelectrospinning of core-shell nanofibers is a modification of the electrospinning process and consists of two coaxially arranged syringe tips, which are both connected to the high voltage source. Two liquids containing the core and shell materials are pumped separately via the two coaxial syringe tips. The resulting nanofiber exhibits a core-shell morphology.

In Fig. 12.3, three different electrospinning techniques, including blend, coaxial, and emulsion electrospinning are depicted. In case A., a uniform nanofiber with additions of a corrosion inhibitor is obtained by conventional electrospinning. In case B., a core-shell nanostructure is obtained with coaxial electrospinning; the corrosion inhibitor is contained in the core of the nanostructure. In case C., a core-shell nanostructure is obtained by conventional electrospinning, when a suitable emulsion is used.

A proper embedding of core-shell nanofibers into the coatings is required to make a coherent coating which adheres very well and securely to the substrate. A proper embedding within the coating matrix can be performed by electrospinning the fibers directly onto the metal substrate or onto the metal substrate already coated with a protective polymer coating. Once this is achieved, the top of the electrospun fiber mat is infiltrated and coated with a suitable polymer. Alternatively, the electrospun nanofibers can be directly deposited into a still wet polymer coating thereby forming after the final polymerization step a solid composite of nanofibers contained in a polymer matrix.

The fabrication of core-shell nanostructures has recently been extensively reviewed by Wang et al. [36]. Core-shell nanofibers are not only a laboratory curiosity but industrial

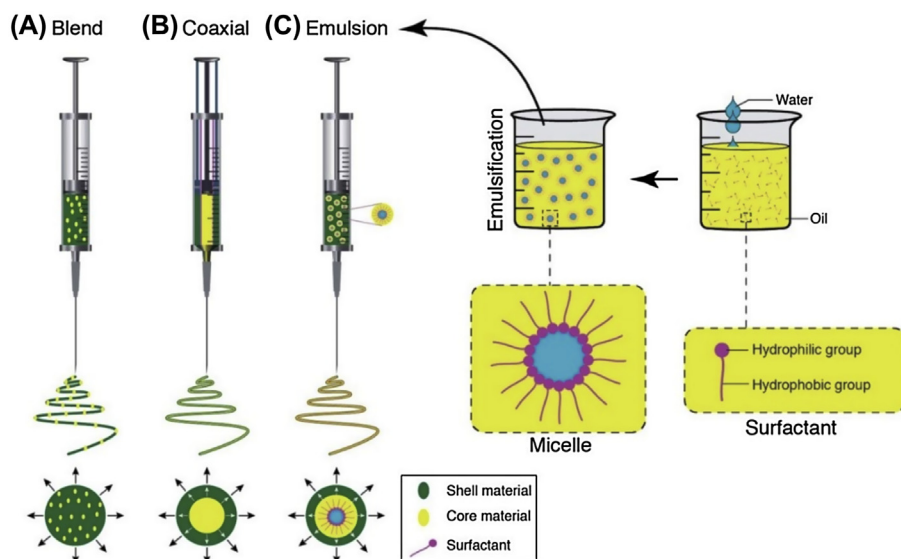


FIGURE 12.3 Schematic displays of the spinneret loaded with a corrosion inhibitor for (A) blend, (B) coaxial, and (C) emulsion electrospinning. Reproduced from N. Nikmaram, S. Roohinejad, S. Hashemi, M. Koubaa, F.J. Barba, A. Abbaspourrad, R. Greiner, *Emulsion-based systems for fabrication of electrospun nanofibers: food, pharmaceutical and biomedical applications*, *RSC Adv.* 7 (2017) 28951–28964 published by the Royal Society of Chemistry.



production processes and devices already available for mass production (e.g., Fluidnatek by Bioinicia [37]). However, the most promising process to produce core–shell nanofibers industrially is the process of solution blowing. The core–shell solution blowing, which has already been scaled to industrial level turns out to be at least 10 times faster than core–shell electrospinning [38,39]. The core-to shell mass ratio can be up to 33 times higher [39] than the core to shell mass ratio achievable by core–shell electrospinning. Lee et al. [39] used poly(vinylidene difluoride) (PVDF) as the shell material. A binary epoxy resin or its hardener was used as the core material. Coaxial solution–blown core–shell microfibers with a shell diameter of 0.2–2.6  $\mu\text{m}$  have been produced [39].

### 3.3 Specific examples of self-healing coatings based on core–shell nanofibers and nanotubes for corrosion protection

Several examples of the use of core–shell nanofibers for the encapsulation of a corrosion inhibitor in the core are described below in greater detail.

A self-healing anticorrosive agent, linseed oil, was encapsulated in a PAN shell by core–shell coaxial electrospinning [40]. The PAN shell was reinforced further with graphene oxide to increase the thermal stability of the shells. The core–shell nanofibers were embedded in polyurethane (PU) coatings to obtain a self-healing effect. The self-healing properties of the scratched coatings were observed morphologically and electrochemically. As a result, the corrosion current density of the coatings with 89 wt.% electrospun fibers was four orders of magnitudes lower than that of pure PU coatings.

Core–shell nanofibers with a core of the corrosion inhibitor MBT in epoxy composite coatings were tested for protection against corrosion of Q345 steel substrates [41]. The PVA/PVDF core–shell nanofibers were prepared by coaxial electrospinning. The Scanning Kelvin Probe (SKP) technique was used to evaluate the corrosion potential in the scratched area of the coatings.

It is worth to mention a rapidly growing interest in the corrosion-protective coatings with multifunctional nanocontainers. Namely, such coatings involve nanocontainers with multiple functionalities based either on the shell sensitive to two or more triggers (e.g., pH, temperature), or combination of primary functionality of the core with the second (different) functionality of the shell. One of the most developed combinations is the use of several corrosion inhibitors in one nanocontainer. In a recent work of Xiaohong [42], pH-responsive self-healing core–shell electrospun nanofibers encapsulating oleic acid (OA) and benzotriazole (BTA) corrosion inhibitors were synthesized for the corrosion protection of carbon steels. The shell of electrospun nanofibers was PVA, and the healing agents OA and BTA were used as core material. The average nanofiber diameters were 350 nm. Furthermore, Jiang et al. [43] reported a dual-responsive multicompartment nanostructure, designed by embedding redox-responsive nanocapsules in pH-responsive nanofibers by colloid-electrospinning. Transmission electron microscopy (TEM) and SEM images of such multicompartment nanofibers are presented in Fig. 12.4.

Redox-responsive silica nanocapsules (SiNCs) were synthesized by using miniemulsion droplets as templates for the hydrolysis and condensation of tetraethoxysilane (TEOS) and an alkoxy silane containing tetrasulfide bonds (TESPT). The encapsulated corrosion inhibitor

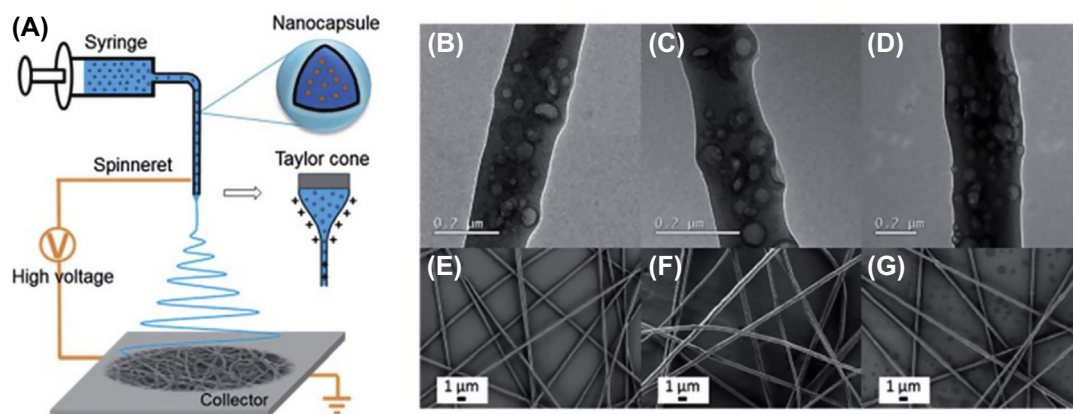


FIGURE 12.4 (A) Schematic illustration of the preparation of multicompartiment nanofibers; (B–D) TEM and (E–G) SEM micrographs of nanofibers with different ratios of PAA and polyvinyl alcohol. *Reproduced from S. Jiang, L.-P. Lv, K. Landfester, D. Crespy, Dual-responsive multicompartiment nanofibers for controlled release of payloads, RSC Adv. 6 (2016) 43767–43770 published by the Royal Society of Chemistry.*

MBT was dissolved in the organic liquid forming the droplets and is hence directly encapsulated in the core of the nanocontainers. The SiNCs were then electrospun in the presence of aqueous polymer solutions to form materials composed of the nanocapsules embedded in hydrophilic nanofibers [43]. Such a system needs to be simultaneously activated by two different stimuli (pH and redox potential change), thus preventing unnecessary leakage of the payload if only one stimulus is activated.

Recent additional examples of core–shell nanofibers usage for self-healing action in anti-corrosive coatings are reviewed in Ref. [44].

## 4. Nanolayers

### 4.1 General aspects of corrosion inhibition with nanolayers

There are two types of ion-exchange release mechanism when considering layered nanoclays as corrosion inhibitor nanocontainers: (1) cation-exchange release and (2) anion-exchange release [45]. Schematic presentation of the layered nanoclay structure is given in Fig. 12.5.

The cation-exchanger clays are less studied in comparison with the anion-exchanger clays [31]. The known issue is that the cation-exchanger clays may suffer from the uncontrolled inhibitor release. Surrounding metal cations necessary to trigger corrosion inhibitor release in cation-exchanger clays may not be directly related to the corrosion process.

Layered double hydroxides (LDHs) belong to the anion-exchanger type of clay minerals. The thickness of the LDH plates is usually about 30–50 nm [31]. The LDH structure consists of stacked layers of positively charged metal hydroxides between which anionic and solvent molecules are intercalated. The anions located in the interlayer can be in general easily replaced. Because of their ability to exchange anions and their unique ultralarge inner surface

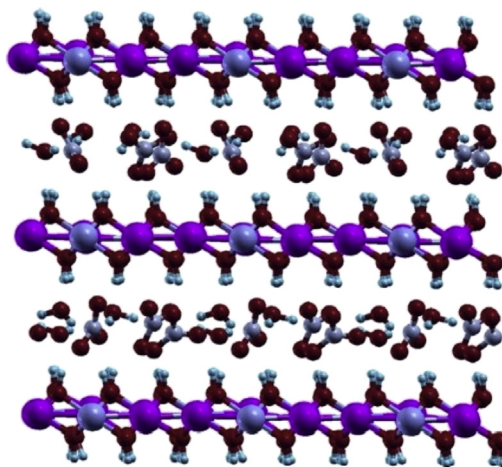


FIGURE 12.5 Schematic presentation of the layered nanoclay structure [31]. Inhibitor molecules (small) are loaded within interlayer galleries between nanoclay layers. *Reproduced from E. Shchukina, H. Wang, D.G. Shchukin, Nanocontainer-based self-healing coatings: current progress and future perspectives, Chem. Commun. 55 (2019) 3859–3867 published by the Royal Society of Chemistry.*

area, LDHs can be used as nanocontainers for releasing an ionic corrosion inhibitor. Additionally, due to their 2D geometries with high aspect ratios, LDHs could enhance the barrier properties of the protective coatings.

The ion-exchange nanoclays are generally abundant and cheap, and this makes them good candidates for application in industrial self-healing anticorrosion coatings. However, the main disadvantage is their low inhibitor loading capacity (5–8 wt.%), due to their small inner lumen (0.5–2 nm) available between the layers [31].

PEs are polymers carrying either positively or negatively charged ionizable groups [46]. An important feature of PEs is that they can be self-assembled into thin films of polyelectrolyte multilayers (PEMs) by using earlier-mentioned LbL assembly technique (18.2.2.). The direct deposition of PEMs/inhibitor complex onto the metal surface, where corrosion inhibitor is sandwiched (complexed) between the alternating PEMs, could offer another practical, fast, and cost-effective approach for the preparation of protective, self-healing coatings. The thickness of such coating can be adjusted by controlling the number of LbL deposition steps. A key feature of PEMs in this case is their ability to interact with a variety of organic/inorganic molecules through electrostatic interactions (complexations) and hydrogen bonding, which allows for loading of variety of corrosion inhibitors between the alternating PEMs [47]. Controllable and on-demand release of corrosion inhibitors is possible upon breaking of the weak noncovalent bonds (e.g., electrostatic/ions cross-links, hydrogen bonding, or hydrophobic associations). Three mechanisms for self-healing of the protective coating based on the PEMs are (1) the intrinsic self-healing triggered by water wettability, (2) the pH-responsive mechanism triggered by the presence of weak ionizable functional groups, and (3) the release of loaded corrosion inhibitor upon swelling of PEMs [47].

## 4.2 Specific examples of self-healing coatings based on nanolayers

Just recently, a novel approach for achieving an active corrosion protection by means of LDH conversion sealing for plasma electrolytic oxidation (PEO) coatings, regardless of PEO coating morphology and phase composition, was demonstrated by Bouali et al. [48]. The authors formed aluminum oxide consisting xerogel in the PEO pores via intermediate sol-gel treatment step. LDH nanocontainers were loaded with vanadate as a corrosion inhibitor. The PEO/LDH hybrid coatings showed an improvement in terms of active corrosion protection, as demonstrated by EIS and SVET analysis.

The addition of a mixture of LDHs and cerium molybdate nanocontainers, both loaded with mercaptobenzothiazole into epoxy primers demonstrated almost negligible corrosion activity after 40 h of immersion into 0.05 M NaCl solution [49]. These results demonstrate beneficial synergetic inhibition effect that combines early corrosion protection and longer-term inhibition.

Ultrasonically activated metal surfaces are called “surface sponges.” They possess large number of active oxygen species allowing formation of superhydrophobic surfaces with superior anticorrosion properties when treated with different chemical agents [50]. The “surface sponges” exhibit mesoporous morphology, high roughness, and an improved adhesion property. The corrosion inhibitor can be loaded into the “surface sponges” via two different approaches: (1) direct chemisorption into the etched metal surface, followed by complexation with oppositely charged PEMs [51] and (2) spray deposition between the alternating PEMs to form a PE/inhibitor sandwich-like nanostructures [52].

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## 5. Porous nanostructures

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### 5.1 General aspects of corrosion inhibition with porous nanostructures

The porous structure of many natural minerals (hydrotalcites, zeolites, clay minerals) allows their use as corrosion inhibitor carriers [53]. The saturation of porous nanostructures with corrosion inhibitors depends on the type of ion exchange (cationic, anionic) for a chosen material. In addition to natural minerals, other porous, commercially available nanostructures have been employed as well as inhibitor containers: mesoporous SiO<sub>2</sub> [54], mesoporous ZrO<sub>2</sub> [55], TiO<sub>2</sub> [56], montmorillonite nanoparticles [57], and graphene oxide [58]. Among these materials, mesoporous SiO<sub>2</sub> has the highest reported inhibitor loading capacity (~80 wt.% [59]) because of its very large specific surface area (>1000 m<sup>2</sup>/g [60]) [10].

The great advantage of porous nanoparticles as nanocontainers is generally their small size (mostly under 1 μm). For this reason, they can be uniformly distributed in thin organic coatings or in sol-gel pretreatments [10]. Moreover, most of the porous nanoparticles can be modified by surface grafting or coating, in order to provide an active inhibitor release in response to different environmental stimuli [61]. This advantage may also be a necessary measure when it comes to porous inorganic nanostructures. Namely, the poor compatibility between organic coating and the inert nanoparticle surface may represent the serious limitation of their direct incorporation. This is especially noticeable if the particles are positioned very close to the metal substrate [62], since the particle agglomeration and defects at the

particle/coating interface may affect coating's barrier and adhesion properties [10]. These issues can be mitigated or even resolved by decorating the surface of the inorganic nanoparticles with organic molecules.

## 5.2 Specific examples of self-healing coatings based on porous nanostructures

Several independent studies revealed that the zeolites can be used successfully as the corrosion inhibitor carriers integrated in sol-gel coatings for self-healing purposes [63–65]. Various corrosion inhibitors have been used:  $\text{Ce}^{3+}$ ,  $\text{Zn}^{2+}$ , as well as mixtures of La + Mo and Ce + Mo, to name a few. Considerable improvement in anticorrosion performance was achieved in sol-gel coatings containing zeolite nanocontainers enriched with mixture of cerium and molybdate nanoparticles, as well as zeolite nanoparticles double-doped with  $\text{Zn}^{2+}$  and mercaptobenzimidazole. In the latter one [65], released inhibitors reduced the corrosion current density from 13.9 to 1.5  $\mu\text{A}/\text{cm}^2$ , after 24 h exposure.

A series of study by Fu et al. [66–69] involves hollow mesoporous silica nanoparticles filled with BTA that can autonomously respond to more sophisticated environmental triggers using supramolecular chemistry. The mesoporous silica nanoparticles were grafted with acid/alkaline dual-responsive supramolecular nanovalves. The assembled nanoparticles (equal amounts of alkaline- and acid-responsive nanocontainers) were directly doped in a sol-gel pretreatment layer on AA2024. The approach demonstrated superior self-healing performance over a wider pH range.

# 6. Corrosion inhibition mechanisms

## 6.1 pH-sensitive nanocapsules

The most used triggering mechanism for the release of corrosion inhibitors from nanocontainers is the local change in the pH value due to anodic and cathodic reactions in the corroding damaged area of the coating. For example, PANI capsules were loaded with MBT (2-mercaptobenzothiazole) corrosion inhibitor and embedded into an epoxy ester coating on AA2024-T3 [70]. For investigation of the release rate in dependence of the pH, the capsules were placed in dialysis bags and exposed to solutions with different pH (1, 5, 7, and 11). By using UV-VIS spectroscopy, it could be confirmed that at alkaline pH the MBT inhibitor was released and under neutral and acidic pH the release was suppressed. This result could further be confirmed by SERS (surface-enhanced Raman spectroscopy). Tavandashti et al. [71] investigated pH-responsive Ce (III) polyaniline nanofibers, embedded in an epoxy matrix for corrosion protection of AA2024-T3. The polyaniline nanofibers were synthesized by soft template method described in a previous paper [72].  $\beta$ -Naphthalene sulfonic acid (b-NSA) was used as a surfactant molecule, which has an amphiphilic structure, which forms in water micelles. In the acidified solution of b-NSA, aniline monomer, and cerium nitrate, the oxidant (ammonium peroxydisulfate) was added. After polymerization, the polyaniline nanofibers were in the emeraldine salt form. The authors claimed that the Ce (III) ions make a complex with the amine groups in the

polyaniline structure. Nitrate ions and b-NSA anions compensate the positive charges from the imine groups. It could be observed that the release of Ce (III) ions is triggered in acid and alkaline solutions. In neutral solution, the release is suppressed. The authors explain this by the breaking of the Ce (III)-PANI complex at high or low pH.  $\text{Ce}^{3+}$  is an excellent corrosion inhibitor for AA-2024-T3. During corrosion,  $\text{Ce}^{3+}$  ions forms cerium oxide or hydroxides on the cathodic sites (e.g., S phase intermetallic), which inhibits the oxygen reduction and therefore reduces the corrosion rate significantly [73–75].

## 6.2 Cationic nanocontainers

Nanocontainers based on nanoclay (e.g., halloysites, montmorillonite, nanozeolites [76]) are known as an effective host for cationic inhibitors. These substances are negatively charged, therefore only cations could be exchanged and intercalated in the host structure. Zeolites are microporous aluminosilicate crystalline particles, exhibiting a three-dimensional (3D) framework which consists of sodalite cages connected through hexagonal prisms. Zeolites possess a negative surface charge. This negative charge is compensated by cations loosely bonded to their framework [77,78]. Cationic active species such as  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  [64,79,80] ions can be entrapped within the structural cages of zeolite particles via a cation exchange process. The release process of the entrapped inhibitors in such containers is stimulated by corrosion activities involving pH changes and presence of cationic species ( $\text{Mn}^+$  and  $\text{H}^+$ ). Selective leaching of the inhibiting ions to the damage site can reinforce the protective oxide layer, guaranteeing a long-term protection of the metallic substrate. Combination of  $\text{Ce}^{3+}$ - and  $\text{La}^{3+}$ -loaded zeolites in corrosion-protective coatings has led to an improved active protection as a result of synergy between the two employed inhibitors [63]. Successive loading of two different inhibitors ( $\text{Ce}^{3+}$  and diethyldithiocarbamate (DEDTC)) in a single zeolite carrier has also been reported with promising results based on a two-step/two-trigger release concept [81]. The organic–inorganic hybrid coatings containing such carriers exhibited a noticeable improvement in active protection of AA2024 compared to protection schemes of single inhibitor-loaded zeolites. Manasa et al. investigated halloysite nanotubes loaded with  $\text{Ce}^{3+}$  and  $\text{Zr}^{4+}$  dispersed in a sol–gel silica matrix applied on A3560 [82]. By embedding the nanotubes without inhibitors in the sol–gel matrix, the barrier properties were significantly reduced and therefore also the corrosion protection. In combination with inhibitors the corrosion protection could be enhanced, and the self-healing property was positively proved by SVET and EIS analysis on scribed samples.

## 6.3 Anionic nanocontainers

Anionic exchanging nanocontainers are positively charged and only anions are exchanged. In contrast to cationic nanocontainers, anionic nanocontainers not only can support the inhibitor release but also can suppress corrosion by trapping of aggressive ions like halides from the corrosive environment into the host matrix. The abovementioned LDHs (26.4.1) can be described by the general formula  $[\text{M}_{1-x}^{2+} \text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \text{mH}_2\text{O}$ , where the divalent



and trivalent cations occupy the octahedral positions within the hydroxide layers [83] and  $x$  is the mol ratio  $M^{3+}/M^{2+}+M^{3+}$  and  $m$  is the number of associated water molecules [84]. The anions  $[A^{m-}]$  are intercalated between the hydroxide layer without any covalent bond to the lamellar structure. The size and the orientation of the anions determine the interlayer distance [84]. A common procedure for the synthesis of LDHs is a two-step procedure [85]. First LDH precursors are produced with easy exchangeable single-charged  $NO_3^-$  ions and then the  $NO_3^-$  will be substituted with suitable organic or inorganic inhibitors in a second ion-exchange reaction. As organic inhibitors, quinaldate, MBT [85], BTA, ethyl xanthate, oxalate [86], imidazole [87] and as inorganic inhibitors, molybdate [88,89], phosphate [90], tungstate ( $WO_3^{2-}$ ) [91], vanadate [92] were used.

#### 6.4 Redox-active nanocontainers

The trigger for the release of corrosion inhibitors in redox-active smart coatings is the change in the electrochemical potential, which happens during the corrosion process. It is well known that redox-active conducting polymers (CP), like polyaniline or polypyrrole have positive charges on the polymer backbone and anions act as countercharges in the doped state. These anions could be a corrosion inhibitor. In case of corrosion, the conducting polymer will be reduced and the inhibitor (anion) will be released. Unfortunately, based on the ionic mobility of the inhibitor, it is also possible that the conducting polymer incorporate cations instead of releasing the inhibitor. In case of fast cation incorporation, even enhanced corrosion could be observed. Vimalanandan et al. [93] developed polyaniline nanocapsules, where the doped polyaniline (dodecyl-sulfate) represents the shell and in the core the corrosion inhibitor is situated to prevent zinc corrosion. Due to the large volume of the dodecyl-sulfate ions and therefore the resulting immobility in the polymer matrix, the charge compensation of the conducting polymer during oxidation and reduction processes are mainly performed by the migration of cations. During reduction of the polymer, cations are incorporated, which changes the volume and increases the permeability of the shell. This enables the inhibitor molecules to diffuse through the polymer shell. To prevent Fermi level alignment, gold nanoparticles were deposited on the PANI shell, and 3-nitrosalicylic acid as corrosion inhibitor was encapsulated. Galvanized steel was coated with a poly(vinyl) butyral-co-vinylalcohol-co-vinylacetate matrix with embedded PANI nanocapsules with 3-nitrosalicylic acid as inhibitor. The self-healing and the delamination behavior of the coating were investigated by SKP (Scanning Kelvin Probe) on scribed samples. It could be demonstrated that the described system is capable of self-healing and prevents delamination. Shuangqing et al. [94] prepared redox-responsive hollow mesoporous silica spheres for encapsulation of corrosion inhibitors. Due to the many and large cavities in the hollow mesoporous silica spheres, a great amount of inhibitor could be loaded. Several methods are suggested to modify the nanocontainer shell, in order to block the corrosion inhibitor release channels [55,95]. By an external stimulus like light, pH, or ion concentration change, the inhibitors will be released. In this work, channels were blocked with ZnO quantum dots, which were bond to the silica spheres through a conjugated disulfide-amide bond. It could be shown that under reducing conditions, the disulfide bonds break and the corrosion inhibitor (MBT) is released.

## 6.5 Light-responsive nanocontainers

Another interesting approach for controllable corrosion inhibitor release was suggested by Skorb et al. [96–98]. Photo-controllable coatings based on light-sensitive nanocontainers were developed and tested. Mesoporous TiO<sub>2</sub> was used as light-sensitive core of the nanocontainers, filled with a corrosion inhibitor (BTA). A PE shell of polyethyleneimine and poly(sodium-4-styrenesulfonate) was subsequently applied onto the TiO<sub>2</sub> cores via LbL assembly technique. The hybrid PE nanocontainers were embedded in an epoxy functionalized sol-gel derived SiO<sub>x</sub>-ZrO<sub>x</sub> matrix. It could be shown that the inhibitor release was triggered by the UV light and pH change. Due to the pH change triggered by corrosion, conformational changes in the polymeric shell were induced, driven by the photocatalytic processes at the TiO<sub>2</sub> core surface. As a result, irreversible decomposition of the PE shell occurred, and the inhibitor was released in the environment.

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## 7. Outlook

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Global loss by corrosion amounts to 2.5 trillion USD [99], which is equivalent to 3.4% of the global GDP (gross domestic product). Corrosion-protective coatings on metallic structures, appliances, and vehicles are used widely in order to counteract such huge losses caused by corrosion. The high demand for corrosion-preventive coatings results in a huge market potential. The global corrosion-protective coatings market size was 14.97 billion USD in 2015 [100]. Innovative corrosion-preventive coatings based on innovative materials with self-healing features are promising further savings on corrosion losses if they can provide at acceptable costs and beneficial properties like effectiveness of corrosion prevention for increased time spans. The presented self-healing solutions for corrosion-preventive coatings are impressively manifold and elaborated, as has been outlined in detail in the previous parts of this chapter. However, the TRL level of most of the presented results is still rather low (TRL 1–3), they are still mostly performed in laboratory and on small coupon sample level only. More industrially related work needs to be invested in order to mature the innovative potential for practical applications. Besides the cost of the materials and of the required (additional) processing steps, which is always a major issue when an innovative solution is competing against state-of-the-art solutions, the beneficial properties of self-healing corrosion prevention coatings must be investigated and secured on longer time scales. State-of-the-art corrosion prevention coatings can sustain their anticorrosion potential for years and in some cases even for decades. Properties of self-healing coating formulations should be investigated on their ability to retain them on similar long time scales. The question must be clarified, if the rather reactive chemicals used for corrosion prevention in the nanosized containers can be securely preserved for a long time span, do not escape and do not react with other coating ingredients in the long term. Such a stability needs to be maintained despite triggering events like heating, freezing, thermal cycling, oxidation, UV degradation, humidity, diffusion of molecular species from the surface or within the coating, etc.

There is a tendency in state-of-the-art corrosion-preventive coatings to make them as thin as possible, due to weight and material savings and esthetical appearance. This might favor the use of smaller nanocontainers versus the use of larger microcontainers in the coating.

But the question has still to be answered if smart coatings made with small nanocontainers can still yield the smoothness and esthetical appearance required not only as freshly deposited coatings, but also in the long run despite severe environmental influences (thermal and mechanical fatigue, etc.)

The toxicity and environmentally friendliness of the new materials need to be elucidated, and considerations must be performed concerning end-of-life scenarios. Standardized industrial tests must be worked out for characterizing and measuring the self-healing effectiveness in order to compare and evaluate quantitatively the beneficial self-healing properties of the different solutions proposed. The added benefits and improved properties of such improved corrosion protection coatings with self-healing properties must be of enough relevance to make such processes industrially and commercially viable. Therefore, it is expected that such improved coatings will be used first on substrates and devices of particularly high value and of low application volume before such solutions can be developed into applications for a larger mass market. Time will surely come for innovative self-healing corrosion-prevention coatings, which mimic in a fascinating way the biological principle of self-repair and self-healing; but there is still a great workload of technology development to be done before such innovative solutions are sufficiently mature for the expected application markets.

Possible industrial applications for smart coatings for corrosion protection are expected to happen first within aerospace, automotive, electronics, construction, and energy industry [101]. Such a market share will still constitute a small percentage of the huge total market of corrosion-protective coatings. The global market in 2027 for self-healing coatings is estimated to be 688 million USD, of which the largest shares will belong to the automotive (164 million USD) and aerospace sector (132 million USD) [101].

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