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## Mesoporous silica nanoparticles as carriers of active agents for smart anticorrosive organic coatings: a critical review

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Mesoporous silica nanoparticles (MSN) have attracted increasing interest for their applicability as smart nanocarriers of corrosion inhibitors, due to their porous structure, resistance to main corrosive environments and good compatibility with polymer coatings. In this review, the main synthetic routes to obtain MSN with tailored textural properties, the design of different loading and stimuli-induced release strategies, the development of advanced organic nanocomposite coatings with MSN and the validation of their anticorrosive performances are reviewed and compared. Through a critical analysis of the literature, the most promising research trends and perspectives to exploit the highly interesting properties of MSN in advanced organic coatings are proposed.

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### Introduction

Corrosion includes a wide range of chemical processes occurring on metal substrates, able to promote the metal degradation and affect their overall properties.<sup>1</sup> Therefore, the prevention of corrosion processes in metallic structures is a pivotal topic to ensure an improvement in their long-term durability. Several strategies are pursued to inhibit or slow down the corrosion, such as the design and development of innovative materials and protective coatings.<sup>2,3</sup> For example, approaches based on chromium-loaded coatings are largely exploited in the aerospace field, but health safety issues are strongly pushing to restrict their use.<sup>4</sup> An alternative strategy is based on anticorrosive coatings realized by directly embedding corrosion inhibitors within the coatings or, more recently, by loading the corrosion inhibitors into nanocarriers which are then dispersed in nanocomposite coatings.<sup>5</sup> This latter strategy is very promising since, by properly designing the nanocomposite coatings and by tailoring their hierarchical organization from nano to macro-scale, it is possible to realize smart anticorrosive systems that effectively exploit the peculiar high specific surface area of nanostructured materials.

Generally, difficult and expensive syntheses are needed to produce polymeric carriers, which in several cases can also show chemical incompatibility with the inhibitors.<sup>6</sup> Therefore,

high surface area inorganic nanocarriers are very attractive as smart corrosion inhibitors nanocontainers and, among them, mesoporous silica nanoparticles (MSN) have a prominent role in the design of innovative and smart nanocomposite coatings.

MSN are a class of materials widely investigated for several applications, ranging from energy storage,<sup>7,8</sup> water and air purification,<sup>9–14</sup> catalysis<sup>15,16</sup> optoelectronics,<sup>17</sup> drug delivery<sup>18,19</sup> or smart release of active agents.<sup>20–22</sup> For coating applications, MSN have several advantages, such as a chemically stable structure, low reactivity and compatibility with numerous matrices.<sup>6,23</sup> Moreover, MSN are currently quite easily synthesized<sup>24</sup> and their high surface area and mesoporous structure are very attractive for adsorption and desorption related applications. Indeed, adsorption is a phenomenon involving the enrichment of a fluid on the surface of an adsorbent, and thus, the most important requirement for a good adsorbent is a large specific surface area. Whether adsorption is induced by long-range interactions (physisorption) or by chemical interactions, such as covalent or ionic bonds (chemisorption), the porosity of the adsorbents outlines their adsorption properties. Physical adsorption, in particular, is favoured in pores whose dimensions are comparable to the adsorptive molecular radius and, for this reason, materials prevalently characterized by micropores and small mesopores are typically considered good adsorbents.<sup>25–27</sup>

However, when MSN are employed as nanocontainers of anticorrosive agents in high performance coatings, both the loading of active agents and their stimuli-responsive release must be carefully investigated. In order to maximize the

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loading of the corrosion inhibitors into the porous nanocarriers, various approaches can be followed. First of all, inhibitor dimension and chemistry have to be considered. The nanocarrier porosity should be tailored in order to contain sufficient amount of active agents and to ease the penetration of the inhibitor into the porous structure.<sup>28–32</sup> Loading capability is a fundamental point to ensure a promising anticorrosive behaviour of the smart system. Moreover, the chemical interactions between the nanocarrier and the inhibitor have to be properly designed and tailored, in order to promote the inhibitor release at the right moment.<sup>33,34</sup> Indeed, nanocarriers must contain the loaded inhibitor for a reasonable time and have a stable chemical structure in the environment wherein they are applied.<sup>35</sup>

As it will be detailed in the next sections of this review, the competitive advantages of coatings realized by embedding MSN as corrosion inhibitors nanocarriers over coatings containing free corrosion inhibitors can be ascribed to the following MSN key properties:

(1) Due to their high porosity, MSN can load high amounts of active agents (*i.e.* anticorrosive agents), allowing to overcome their solubility limit when used in polymeric coatings;

(2) Various corrosion inhibitors can be loaded into MSN, almost irrespectively on their chemical nature and properly selected on the basis of the degradation mechanism of the substrate to be protected;

(3) By loading the corrosion inhibitors into MSN, also active agents that are not miscible with the coatings polymer matrices can be used;

(4) Tailored capping systems can be designed to minimize the early release of the corrosion inhibitors from MSN and widely modulate the release kinetics;

(5) Engineered MSN-based systems can be designed to promote the stimuli-responsive release of the corrosion inhibitors under selected conditions (such as pH variations);

(6) MSN can protect the corrosion inhibitors from degradation, such as UV-induced or high temperature-induced degradation;

(7) MSN can be properly functionalized to promote their compatibility (both enhancing dispersion and interfacial interactions) with organic coatings, improving functional and structural (*e.g.* mechanical, adhesion, indentation resistance) properties;

(8) Finally, when engineered MSN are effectively embedded in protective coatings, they contribute to maximize both the anticorrosive properties through active (*e.g.* stimuli-responsive release of anticorrosive agents) and passive mechanisms (*e.g.* hindering the movement of aggressive species).

To confirm the above points, in this work, the main approaches for the synthesis of MSN as nanocarriers of corrosion inhibitors with tailored textural properties, for the design of different loading/release strategies, and for the use of MSN to realize advanced organic coatings are reviewed and compared. Moreover, results of the application of the obtained smart anticorrosive coatings for the protection of different

metal and alloy substrates used in civil and industrial buildings and infrastructures, transportation, aeronautics and cultural heritage are reported and critically discussed.

## Mesoporous silica nanoparticles (MSN)

MSN represent a versatile and inexpensive kind of nanoreservoir with excellent chemical stability, biocompatibility, controllable pore diameter, easy surface functionalization, high surface area and pore volume.<sup>36–41</sup>

MSN can be synthesized by a modified Stober process,<sup>42</sup> by hydrolysis and condensation of silica precursors.<sup>43</sup> Usually tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS)<sup>44</sup> are used, but also other precursors are often reported. For instance, 3-mercaptopropyltrimethoxysilane (MPTMS) has been used by Sivanandini *et al.*,<sup>45</sup> demonstrating the improved efficiency of this precursor for the MSN synthesis, able to reduce the particles aggregation and improving their geometric uniformity. Moreover, surfactant, micelles forming materials, polymers or other dopants<sup>46–49</sup> are added to the selected precursors.

In particular, the most used surfactant is cetyltrimethylammonium bromide (CTAB)<sup>50–61</sup> although other salts are often exploited, such as hexadecyltrimethylammonium *p*-toluenesulfonate (CTAT), cetyltrimethylammonium chloride (CTAC)<sup>62</sup> and dodecyltrimethylammonium bromide (C<sub>12</sub>TMABr).<sup>44,63,64</sup>

In the mesoporous silica nanoparticles growth, by selecting adequately the pH, the condensation of silicon is enhanced with respect to the Stober process, promoting the formation of Si–O–Si bonds, instead of Si–OH.<sup>65</sup> Then, pores are formed with the template removal in the nanoparticle structure through calcination or by solvent extraction (see Fig. 1).

Many factors concur to determine the MSN porous structure, such as the type of surfactant and the reaction conditions, allowing to control the nanoparticles pores size in the whole range of the mesopores, and, in some cases, also in the

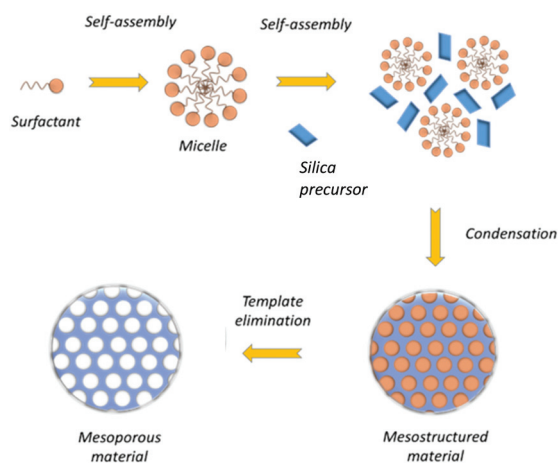


Fig. 1 Schematic representation of the MSN synthesis.



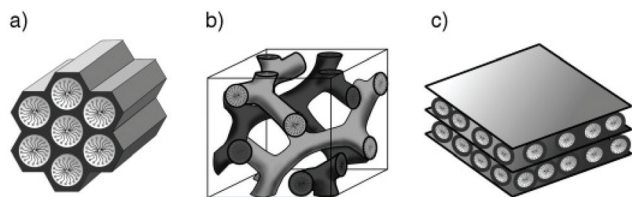


Fig. 2 Hexagonal, cubic and lamellar mesostructures of MCM-41 (a), MCM-48 (b) and MCM-50 (c), respectively. Reprinted with permission from ref. 78. Copyright 2006 John Wiley and sons.

range of the micropores, until the lower limit of about 0.1 nm.<sup>66</sup>

The MSN may have different mesostructures (Fig. 2), some of them take the name from their developers, and are distinguished in:

- Hexagonal, such as the “Mobil Composition of Matter number 41” (MCM-41),<sup>52,57</sup> “Santa Barbara Amorphous type number 15” (SBA-15)<sup>67–69</sup> or “Folded Sheets Mesoporous material number 16” (FSM-16);<sup>70</sup>
- Cubic, such as MCM-48;<sup>71,72</sup>
- Lamellar, such as MCM-50;<sup>73</sup>
- Other random structures,<sup>74</sup> such as the “Technische Universiteit Delft number 1” (TUD-1),<sup>75</sup> the “Hiroshima Mesoporous Material number 33” (HMM-33)<sup>76</sup> and the “Michigan State University type number 1” (MSU-1).<sup>77</sup>

In Table 1 the different mesostructures and textural properties of the above mentioned MSN are summarized.

Among the different types of pores morphology, Zhang *et al.*<sup>24</sup> demonstrated that, by varying the pH of the reaction mixture, so-called stellate, raspberry or worm-like structures can be also obtained (Fig. 3).

Moreover, MSN with a hollow structure (HMSN) can be obtained with the use of proper templates.<sup>79</sup> HMSN can display significantly higher pore volumes than MSN, and for this reason they are very attractive for a wide range of applications.<sup>79</sup> For their synthesis, the templates employed are usually classified in “hard” templates, such as polymeric materials,<sup>80–82</sup> silica,<sup>83</sup> carbon<sup>84</sup> or inorganic salts<sup>85</sup> spheres, or “soft” templates, such as gas bubbles,<sup>86</sup> surfactant

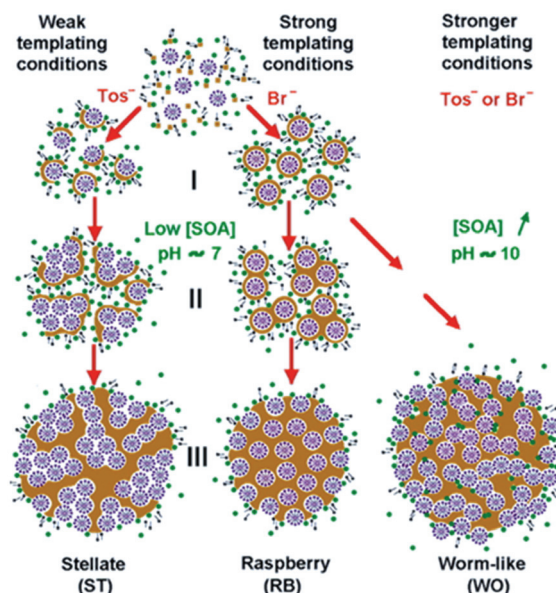


Fig. 3 Reaction conditions for stellate, raspberry and worm-like MSN porous structures obtained at different small organic amines (SOA) concentrations (pH  $\approx$  7 or 10) and with different surfactants (CTAT and CTAB). Reprinted with permission from ref. 24. Copyright 2013 American Chemical Society.

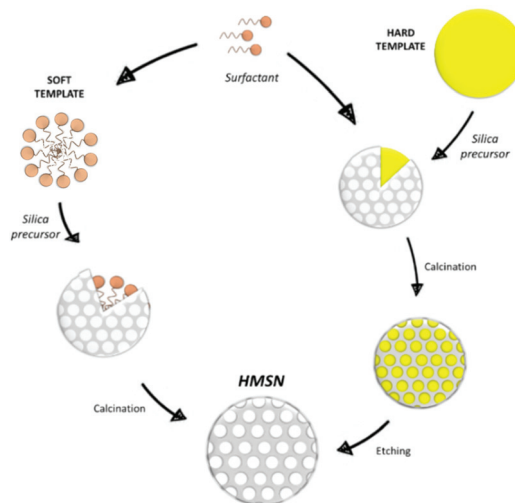


Fig. 4 Hard and soft templating in HMSN synthesis.

micelles,<sup>87–90</sup> vesicle template<sup>91–93</sup> or emulsion or aerosol droplets<sup>94–99</sup> (Fig. 4).

When using surfactant micelles, the difference between HMSN and MSN syntheses mainly consists in the amount of surfactant employed: increasing the surfactant/silica precursor ratio promotes the formation of hollow structures.<sup>88</sup> In the hard template case, a great control in particles growth is guaranteed and an etching treatment is needed to remove the template.<sup>100</sup>

A drawback of this process is that, in some cases, it can cause partial collapse of the hollow structure.<sup>101</sup> On the other

Table 1 Mesostructures and textural properties of MSN

MSN structure	MSN name	Ref.	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore diameter (nm)
Hexagonal	MCM-41	52	1016	3.77
		57	Not reported	<5
	SBA-15	67	789	5.9
		68	550–600	6–10
		69	609	8
Cubic	MCM-48	70	700–1250	1.6–4.5
		71	994–1258	1.45–1.72
Lamellar	MCM-50	72	1331–1464	3.2–3.6
		73	1222	5.6
Random	TUD-1	74	453	4.9
		75	600	5
	HMM-33	76	600	5
		77	891	2.5



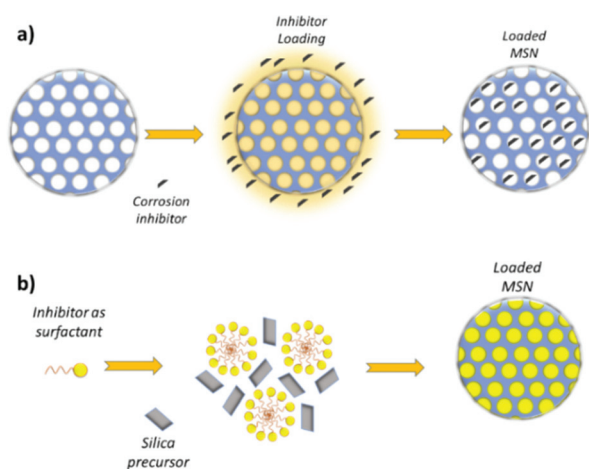
hand, soft templates can be removed by heating, calcination or solvent extraction but, in these cases, the obtainment of homogeneous nanoparticles is more challenging, due to the low rigidity of the template.<sup>79</sup> Finally, a soft-hard template approach, based on the simultaneous presence of a soft and a hard template, can be also pursued for the HMSN synthesis. For example, Zhang *et al.*<sup>102</sup> exploited the combination of carbon nanospheres and CTAB, while Zhu *et al.*<sup>103</sup> and Chenan *et al.*<sup>104</sup> used polyvinylpyrrolidone (PVP) and CTAT or CTAB.

## Loading of corrosion inhibitors into MSN and its effectiveness

In order to employ MSN as smart nanocontainers, several approaches have been designed to maximize the loading of the active molecules while ensuring that their release mainly occur in response to external stimuli. Main strategies applied to realize the corrosion inhibitors loading are presented and discussed in the following sections with a specific focus on pristine MSN, surface modified MSN and organically coated MSN.

### Pristine MSN

One of the most effective approach to load corrosion inhibitors into MSN consists in mixing the nanoparticles with a corrosion inhibitor solution under reduced pressure. The reduced pressure promotes the penetration and physical adsorption of the active molecule into the MSN pores. Then, under proper temperature and pressure conditions, the solvent is evaporated, leaving the corrosion inhibitor into the pores,<sup>105,106,107</sup> Active molecules have also been adsorbed into MSN from solution without vacuum application,<sup>62,108</sup> even if this simplified strategy allows only to load limited amount of corrosion inhibitor, since it is not possible to limit its premature release during the loading procedure.<sup>19</sup> In Fig. 5a a typical active molecule loading into silica mesopores is schematized.



**Fig. 5** Corrosion inhibitor loading into the pores (a) and one-step MSN synthesis and drug loading, wherein the surfactant also acts as the loaded active molecule (b).

Among the investigated corrosion inhibitors loaded into mesostructures, several works focused on benzotriazole (BTA), which is a very effective organic inhibitor with high solubility in water and in organic solvents (*e.g.* acetone)<sup>105,109–112</sup> and mercaptobenzothiazole (MBT), another organic inhibitor insoluble in water and soluble in organic solvent such as ethanol, acetone and ether.<sup>104,108,113–115</sup> Other organic inhibitors are 8-hydroxyquinoline (8-HQ),<sup>106</sup> PVP,<sup>116</sup> hydroxybenzotriazole (HOBt),<sup>62</sup> sulfamethazine<sup>61</sup> and dodecylamine.<sup>117</sup> Some researchers have also developed systems with inorganic corrosion inhibitors. Zea *et al.*<sup>63</sup> proposed the loading of sodium phosphomolybdate ( $\text{Na}_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$ ) in MSN pores as an environment friendly compound. Other inorganics were also exploited, such a cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), proposed by Noiville *et al.*<sup>118</sup>

With another approach, schematized in Fig. 5b, researchers also investigated the possibility to synthesize the MSN and load the corrosion inhibitor in a one-step process. Maia *et al.*<sup>51</sup> first mixed MBT and CTAB, then added TEOS to the mixture and promoted the synthesis of MSN, encapsulating MBT into the synthesized mesopores of the silica nanoparticles. Xu *et al.*<sup>119</sup> followed the same procedure, studying the effect of BTA loading. Jiang *et al.*<sup>120</sup> mixed TEOS, CTAB and cerium chloride ( $\text{CeCl}_3$ ) and synthesized MSN through aerosol assisted evaporation-induced self-assembling (EISA).

Although a single step synthesis and corrosion inhibitor loading is very attractive, the formation of mesopores in presence of corrosion inhibitors could lead to the obtainment of an imperfect porous structure.<sup>120</sup>

In Table 2 the various loading strategies presented in this section are summarized. As shown, the amount of corrosion inhibitor loaded varies in a wide range, approximately from 10 to more than 80 wt% with respect to the weight of MSN. In fact, the amount of loaded corrosion inhibitor depends on the pore size and volume of the nanoparticles and on the corrosion inhibitor molecular dimension. In particular, HMSN have a great potential in active molecules loading, since they show an increased pore volume that allows the loading of higher amount of corrosion inhibitor. In this way, Chenan *et al.*<sup>104</sup> loaded about 72 wt% of MBT into HMSN. In general, then, very high amount of loadings in MSN may be due to surface excess adsorption of molecules in multilayer coverage.

The strategy based on the simple corrosion inhibitor loading is not often followed, due to the difficulty in holding the loaded corrosion inhibitor into the nanoparticle.<sup>121</sup> Therefore, researchers developed several “stopping systems”, based on nanoparticles functionalization with functional groups somehow bound to the corrosion inhibitors or external coatings surrounding the MSN. In most of these cases, the corrosion inhibitor release can be modulated and activated in response to an external trigger.

### Surface modified MSN

The development of surface modified MSN is a widely exploited approach to optimize the loading and modulate the corrosion inhibitor release, and it may interest the internal



Table 2 Pristine MSN loaded with corrosion inhibitors

Corrosion inhibitor loading technique	Ref.	Loaded corrosion inhibitor molecule	Corrosion inhibitor loading content	
MSN synthesis and corrosion inhibitor loading without reduced pressure	62	Hydroxybenzotriazole	40 wt%	
	108	Mercaptobenzothiazole	35 wt%	
	MSN synthesis and reduced pressure corrosion inhibitor loading	61	Sulfamethazine	Not reported
		63	Sodium phosphomolybdate	Not reported
	104	Mercaptobenzothiazole	72 wt%	
	113		20 wt%	
	114		20 wt%	
	115		83.7 wt%	
	105	Benzotriazole	17 wt%	
	106	8-Hydroxyquinoline	77 wt%	
	118	Cerium nitrate hexahydrate	Not reported	
One-step MSN synthesis and corrosion inhibitor loading	51	Mercaptobenzothiazole	10 wt%	
	119	Benzotriazole	16 wt%	
	120	Cerium chloride	Not reported	

surface of the pores and/or their edges. The MSN decoration can be operated during the MSN synthesis<sup>122,123</sup> or after the synthesis<sup>52,54–56,58–60,69,124</sup> and, in some cases, after the corrosion inhibitor loading or grafting.<sup>57,125</sup>

Surface modification is generally operated through organosilanes, that can easily react with the MSN surface. The most used silanes have  $-NH_2$  functionality, in order to impart to silica a basic character and improve its reactivity towards further functionalization. 3-Aminopropyltriethoxysilane (APTES),<sup>55,67,124</sup> (1-(2-aminoethyl)-3-aminopropyltriethoxysilane) (AEAPTMS)<sup>54,56,58–60,122</sup> and 3-trimethoxysilylpropylamine (TMSPA)<sup>52</sup> are among the most used amino precursors. Yeganeh *et al.*, in their works, induced the reaction between amino-functionalized MSN and  $Fe^{3+}$  or  $Al^{3+}$ , by reacting the particles with  $FeCl_3$ <sup>56,58–60,122</sup> and  $AlCl_3$ ,<sup>54</sup> respectively. The presence of the intermediate metal cations  $Fe^{3+}$  or  $Al^{3+}$  was then exploited by several research groups to load the nanoparticles with anionic corrosion inhibitors, such as molybdates<sup>54,58–60,122</sup> or fluorides<sup>56,124</sup> (Fig. 6).

Kermannezhad *et al.*<sup>52</sup> followed similar approaches, using TMSPA to graft 2-mercaptobenzoxazole (MBA). Ashrafi-Shahri *et al.*<sup>55</sup> functionalized MSN with APTES and, in a second step, with  $FeCl_3$ , in order to graft the corrosion inhibitor Eriochrom Black T (EBT,  $C_{20}H_{12}N_3O_7SNa$ ). Amini *et al.*<sup>69</sup> functionalized MSN with piperazine, in order to improve the MBT capability to load the mesopores.

Another highly exploited functionality is based on  $-SH$  groups, which induce an acid character to the nanoparticles, as in the case of MSN functionalized with MPTMS. In this way, Alipour *et al.*<sup>57</sup> exploited MPTMS to improve the efficiency of MSN impregnated with molybdate as a corrosion inhibitor. The authors showed that protective compounds are formed after release of molybdate from mesoporous silica, while the functionalization with MPTMS promoted the self-healing property of the anticorrosive coating by reducing the coating porosity and by increasing the coating hydrophobicity and its compatibility with the metal substrate.

Promoting the hydrophobization by using different silanes was an approach adopted in several works. In order to improve the dispersion of BTA loaded MSN into a polyester-resin based

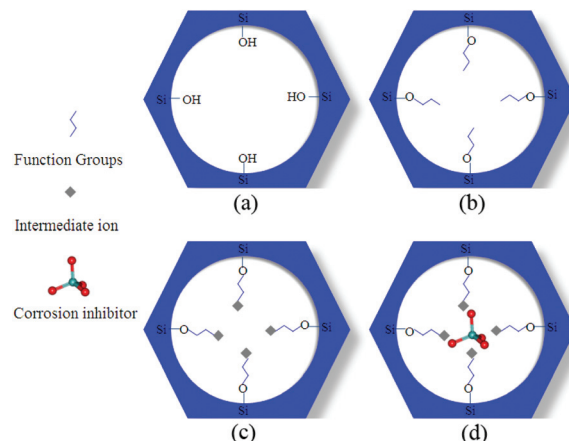


Fig. 6 The three step mechanism exploited to load anionic corrosion inhibitors into MSN: (a) starting MSN; (b) functionalized MSN (treated for instance with amino silanes); (c) amino-functionalized MSN treated with metal cations (such as  $Fe^{3+}$  or  $Al^{3+}$ ); (d) anionic corrosion inhibitors (such as molybdates or fluorides) “entrapped” into MSN pores by coordination chemistry. Reprinted from ref. 58. Copyright 2014, with permission from Elsevier.

coating, Hollamby *et al.*<sup>123</sup> functionalized MSN with octyltriethoxysilane (OTES), while Zhao *et al.*<sup>125</sup> functionalized BTA loaded MSN with dodecyltrimethoxysilane (DTMS) to improve the hydrophobicity of a mesoporous film onto an aluminium alloy substrate.

On the other hand, other MSN functionalizations were pursued with the aim of creating a responsive shell outside the nanoparticles. External stimuli, such as pH changes, redox reactions, temperature gradient and light irradiation, can modify the external shell and induce the corrosion inhibitor release. These shells act as switches, which modify their location, shape or structure in response to stimuli.<sup>126</sup> These switches can have varying complexity. For instance, they can be obtained by molecules directly grafted to MSN or by realizing complex systems, applying non-covalently bonded or mechanically interlocked shells.<sup>126</sup>



Chen *et al.* proposed a one-molecule-grafted approach: during a typical HMSN synthesis, they added 4-phenylazoaniline (4-PhAA), an azobenzene, and also isocyanatopropyltriethoxysilane (ICPES) to graft azobenzene onto HMSN and, then loaded BTA into the nanopores.<sup>5</sup> This switch is ultraviolet (UV) activated, exploiting the *cis/trans* isomerization of azobenzene,<sup>127</sup> which modifies the azobenzene shell onto MSN, thus inducing the BTA release.<sup>47</sup>

Sun *et al.*<sup>128</sup> demonstrated the redox-responsive character of MBT loaded HMSN, capped with zinc oxide (ZnO) through APTES and dithiodipropionic acid (DTPA).

More complex structures were realized by Fu's group, who largely investigated how to functionalize MSN in order to create a pH responsive nanovalve outside the nanoparticle.<sup>129–135</sup> This mechanism is based on the non-covalent interaction between the installed macrocycle and the external surface long chain molecule.<sup>130</sup> Their research focused on cucurbit[*n*]uril (CB[*n*]), macrocyclic molecules used by the authors as a cage.<sup>129–132</sup> In particular, they used CB[7]<sup>129</sup> and CB[6].<sup>130–132</sup> CB[7], hexanediamine (HDA) and ferrocene dicarboxylic acid (FCDCA) composed a pseudorotaxanes grafted outside the HMSN (through chloromethyltriethoxysilane, CMTES), loaded with caffeine, used as corrosion inhibitor.<sup>129</sup> Instead, CB[6] was used in interaction with butanediamine (BDA) and chloropropyltriethoxysilane (CPTES)<sup>130</sup> or CMTES.<sup>131</sup> Moreover, they developed a similar system realized by the simultaneous use of HDA and 1,6-bis(pyridinium)hexane (BPH) as two recognition sites onto HMSN, capped with CB[6].<sup>132</sup> Other supramolecular nanovalves are based on pillararenes (WPs)<sup>133,134</sup> and cyclodextrin (CDs).<sup>131,136</sup> In these systems, the corrosion inhibitor used was BTA,<sup>130–132</sup> 8-HQ,<sup>134</sup> 2-hydroxy-4-methoxy-acetophenone (HMAP)<sup>133</sup> and *p*-coumaric acid (CA).<sup>136</sup>

Furthermore, the corrosion inhibitor can be exploited to realize an external blocking system after its loading into the mesopores. This approach is based on the interaction between the corrosion inhibitor and an external compound, assembling a complex outside the nanopores, which modulate the release rate. Abdullayev *et al.*<sup>137–139</sup> tailored the controlled BTA release from other inorganic carriers (halloysite nanotubes), through its reaction with copper ions, forming a Cu-BTA complex. They exploited the properties of the Cu-BTA complex whose water solubility is pH responsive, obtaining the release of BTA with the decrease of pH. Cu-BTA complexes were also exploited in MSN by Zheng *et al.*<sup>140</sup> and Castaldo *et al.*<sup>141</sup> for self-healing and anticorrosive applications (see Fig. 7).

In Table 3, the results obtained by applying the functionalization approaches described in this section are summarized. As shown, also in this case the loading efficiency ranges from values lower than 1 wt% up to about 25 wt%. To be noted is that, in general, these systems show a lower loading of corrosion inhibitors with respect to the pristine MSN summarized in Table 2. Indeed, a functionalization of the MSN may reduce the surface adsorption sites and/or the pore volume of the nanoparticles, thus reducing the MSN loading capability.

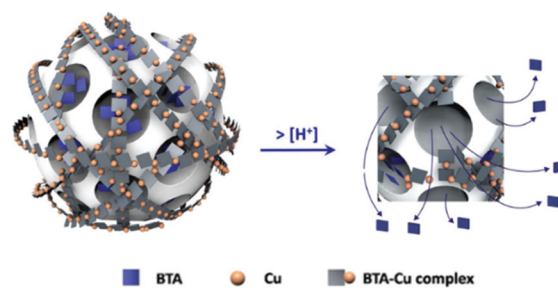


Fig. 7 Scheme of the BTA release in acid solution. Reproduced from ref. 141 Copyright © 2020, Elsevier Masson SAS. All rights reserved.

Moreover, the application of blocking systems may induce the release of part of the loaded active molecules.

### Organically coated MSN

Another approach aimed to modulate the corrosion inhibitors release rate is based on building stimuli responsive coatings around the nanoparticles loaded with the corrosion inhibitors.

These strategies aim to maximize the exploitation of the inner porosity of the nanoparticles for the active molecules loading, developing a stimuli responsive release system on the external surface of the nanoparticles.

For example, layer-by-layer (LbL) deposition of polyelectrolytes is a largely used approach.<sup>68,142–148</sup> Skorb *et al.*<sup>143</sup> developed a pH sensitive polyelectrolyte shell made by a deposition of alternate layers of polyethyleneimine (PEI) and poly(sodium 4-styrenesulfonate) (PSS), enwrapping the corrosion inhibitor 2-(benzothiazol-2-ylsulfanyl)-succinic acid (BYS) into the MSN pores. They also developed a laser-driven release of BTA from MSN coated with the same polyelectrolyte shell.<sup>142</sup> Shi *et al.*<sup>68</sup> and Siva *et al.*<sup>144</sup> realized a PEI/PSS polyelectrolyte layer, encapsulating the corrosion inhibitor 8-HQ and polyaspartic acid (PAA). Zea *et al.*,<sup>146–148</sup> deposited poly(diallyldimethylammonium chloride) (PDDA) pH-responsive polyelectrolyte layers onto HMSN loaded with sodium phosphomolybdate, using sodium chloride (NaCl) to improve the efficiency in the deposition of the polyelectrolyte (Fig. 8).

In details, NaCl enhances the ionic strength, and allows to overcome the electrostatic barrier formed between the deposited polyelectrolyte layers and the bulk molecules in the polymeric solution, and therefore to deposit a higher number of polyelectrolyte layers.

Grigoriev *et al.*<sup>145</sup> developed a system based on MSN loaded with BTA and covered with a polyelectrolyte layer which was in turn complexed with the corrosion inhibitor (BTA), combining a double anti-corrosive effect. The complete structure outside the MSN consisted of PEI/PSS layers, covered with further PSS/BTA complex layers. PEI was also used by Wen *et al.*,<sup>149</sup> which used it to enwrap BTA loaded MSN, previously functionalized with APTES.

The combination of active and passive corrosion protection is a very attractive goal, especially when the corrosion inhibitors nanocarriers are designed for being included into protec-



Table 3 Surface modified MSN loaded with corrosion inhibitors

Functionalization step	External nanovalve (X)	Ref.	Silane modification and other functionalities between MSN and corrosion inhibitor	Corrosion inhibitor	Corrosion inhibitor loading	
During MSN synthesis	X	5	Isocyanatopropyltriethoxysilane, phenylazoaniline	Benzotriazole	25.2 wt%	
		123	Octyltriethoxysilane		1 wt%	
After MSN synthesis and before corrosion inhibitor loading	X	123	Aminoethylaminopropyltriethoxysilane, FeCl <sub>3</sub>	Sodium molybdate	Not reported	
		52	Trimethoxysilylpropylamine	Mercapto-benzoxazole	25 wt%	
		54	Aminoethylaminopropyltriethoxysilane, AlCl <sub>3</sub>	Sodium molybdate	18 wt%	
		58	Aminoethylaminopropyltriethoxysilane, FeCl <sub>3</sub>		18 wt%	
		59			Not reported	
		60			Not reported	
		56		NaF	Not reported	
		124	Aminopropyltriethoxysilane, FeCl <sub>3</sub>		Not reported	
		55		Eriochrom Black T	Not reported	
		69	Piperazine	Mercapto-benzo-thiazole	13 wt%	
		128	Aminopropyltriethoxysilane, dithiodipropionic acid and ZnO		4.1 wt%	
		129	Chloromethyltriethoxysilane, hexanediamine, ferrocene dicarboxylic acid and cucurbituril[7]		Caffeine	20.2 wt%
		130	Chloropropyl-triethoxysilane, butanediamine and cucurbituril[6]		Benzotriazole	64 wt%
		131	Octadecyltrimethoxysilane, chloromethyltriethoxysilane and phenylaminomethyltriethoxysilane, butanediamine, cucurbituril[6] and $\alpha$ -cyclodextrin			11.3 wt%
132	Aminopropyltriethoxysilane, hexanediamine, bispyridiniumhexane and cucurbituril[6]			About 11.6 wt% including the capping agent		
133	Aminopropyltriethoxysilane, ammonium carboxylated pillar[5]arane		Hydroxy-methoxy-acetophenone	12.4 wt%		
134	Mercaptopropyltrimethoxysilane, ammonium carboxylated pillar[5]arane, Fe <sub>3</sub> O <sub>4</sub>		Hydroxyquinoline	0.72 wt%		
136	Aminopropyltriethoxysilane, ferrocenylmethyltriazolylmethyl-heptakisdeoxyiodo- $\beta$ -cyclodextrin		Coumaric acid	15 wt%		
140	Aminopropyltriethoxysilane, CuSO <sub>4</sub>		Benzotriazole	7.3 wt% (by TGA); 6.6 wt% (by UV)		
			Trimethoxysilylpropylethylenediamine, CuSO <sub>4</sub>	8.9 wt% (by TGA); 8.5% wt% (by UV)		
			Trimethoxysilylpropyl-diethylenetriamine, CuSO <sub>4</sub>	8.6 wt% (by TGA); 7 wt% (by UV)		
After MSN synthesis and corrosion inhibitor loading	X	57	Mercaptopropyltrimethoxysilane	Sodium molybdate	10 wt%	
		140	CuSO <sub>4</sub>	Benzotriazole	10.3 wt% (by TGA); 9.2 wt% (by UV)	
		141			20%	

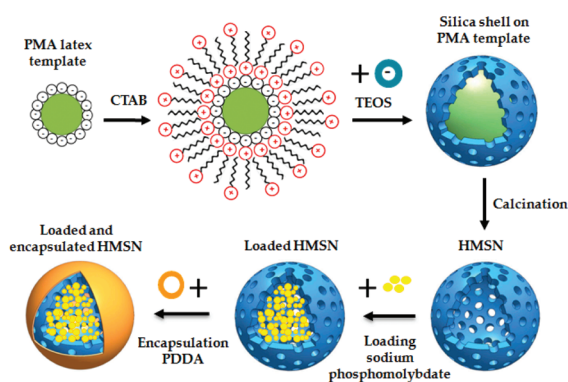


Fig. 8 HMSN synthesis, through hard polystyrene methylacrylic (PMA) template, HMSN loading with sodium phosphomolybdate and polyelectrolyte PDPA coating. Reproduced from Zea *et al.*<sup>146</sup>

For this reason, the possibility to synthesize nanocarriers able to intrinsically create passivating films onto metal surface is very interesting. Wang *et al.*<sup>150</sup> realized BTA loaded MSN modified with a polyaniline (PANI) polyelectrolyte external layer, wherein PANI acts as passive corrosion protection agent. A hard template silica nanoparticle was functionalized with PVP in order to graft aniline, which was polymerized onto the surface of PVP-modified silica. Then, the PANI-modified silica nanoparticles were etched with sodium hydroxide and phosphoric acid and then calcined, obtaining a void PANI-modified silica nanoparticle, thanks to the “protective” effect of PVP that disallowed the complete etching of the silica, promoting the mesoporous structure formation. Finally, BTA was loaded into the obtained system, exploiting its high capability to penetrate into PANI:<sup>151</sup> the



Table 4 Coated MSN loaded with corrosion inhibitors

Coating step	Ref.	Type of coating	Coating structure	Corrosion inhibitor	Corrosion inhibitor loading content	
Before corrosion inhibitor loading	150	Polyelectrolyte layers	Polyvinylpyrrolidone and polyaniline	Benzotriazole	26.9 wt%	
After corrosion inhibitor loading	68		Polyethyleneimine/polystyrene sulphonate	Polyethyleneimine/polystyrene sulphonate + polystyrene sulphonate/benzotriazole	Hydroxyquinoline	8 wt%
	142				Benzothiazolyl-sulfanylsuccinic acid	≈8.5 wt%
	143				Benzotriazole	7.5 wt%
	144				Polyaspartic acid	Not reported
	145				Benzotriazole	
	146				Sodium phosphomolybdate	
	147					
	148					
149	Self-assembled external layers	Aminopropyltriethoxysilane and polyethyleneimine	Aminopropyltriethoxysilane and polyethyleneimine	Benzotriazole	10.09 wt%	
152			Tannic acid-Fe complex	Benzotriazole	Not reported	

peculiarity of this process is that BTA loading is performed after the obtainment of the PANI external layer.

Finally, with another approach, Qian *et al.*<sup>152</sup> reported a pH-responsive capping layer, based on tannic acid (TA)-Fe<sup>3+</sup> complexes, able to coat BTA loaded MSN and act as effective capping agents for the loaded BTA. With the proposed approach, the authors exploited the pH dependent stability of the TA-Fe<sup>3+</sup> complex and the affinity of the complex to the MSN substrates, without any further MSN surface functionalization, avoiding the polyelectrolyte layers deposition.

In Table 4 the results obtained by applying the coating approaches described in this section are summarized. The application of stimuli-responsive coatings is a very promising recent research trend and new highly effective methods, especially those based on the LbL application of smart polyelectrolyte shells, are expected to be exploited in the near future for the controlled release of corrosion inhibitors. However, polyelectrolyte shell application can involve the partial unloading of corrosion inhibitor from mesopores. This can be caused, for example, by the pH conditions during the shell formation, which may induce the release. This is the main reason why, in this case, it is particularly difficult to reach a high amount of loaded inhibitor.

## Corrosion inhibitor triggered release mechanisms

As already showed in the previous section, the main reason why MSN are often functionalized or coated is to control the release of the loaded corrosion inhibitor. This is promoted by an external stimulus, which perturbs the equilibrium of the loaded nanoparticle and triggers the release of the active agent.

### pH-Sensitive systems

One of the most exploited stimuli for corrosion inhibitors release is the pH variation. This triggering is very useful for metal substrates, whose corrosion usually proceeds generating anodic and cathodic regions, with consequent pH decrease or increase. Thus, the realization of nanostructures which involve pH-responsive complexes allows the release of corrosion inhibitors in the corroded area; therefore, a pH-sensitive system can induce a self-healing mechanism once the corrosion process starts.<sup>113</sup> Researchers developed complex systems, tuning the nanocontainers responsiveness with respect to specific conditions, in order to promote the release of the corrosion inhibitors in those conditions typical of specific corrosion mechanisms. Therefore, different studies were focused on the optimization of the corrosion inhibitors release in acid pH, alkaline pH or both of them. In particular, some release studies highlighted how pH affects the electrostatic interaction between MSN and the loaded corrosion inhibitor and therefore promotes or inhibits the corrosion inhibitor release from the MSN pores.<sup>54,113,147</sup>

Different release behaviours are reported on systems based on MBT-loaded MSN: Borisova *et al.*<sup>113</sup> and Rahsepar *et al.*<sup>108</sup> observed a higher release amount of MBT in alkaline conditions, due to the pH dependent solubility of MBT, while Maia *et al.*<sup>51</sup> and Chenan *et al.*<sup>104</sup> verified a faster release in acid environment, due to the hydrolysis of an amount of non-fully hydrolysed TEOS, that, in acid ambient, further hydrolyses and unseals some pores, improving MBT release. They also observed that the maximum corrosion inhibitor release in corrosive environments is reached, after about 5 hours, due to both the solubility of MBT in the solution and the MBT degradation to sub-products, such as 2-hydroxybenzothiazole and benzothiazole.<sup>51,104,113</sup> With a different approach, Amini *et al.*<sup>69</sup> promoted the MBT release in neutral and alkaline conditions by exploiting the interaction between MBT with piperazine, previously grafted onto the MSN surface.

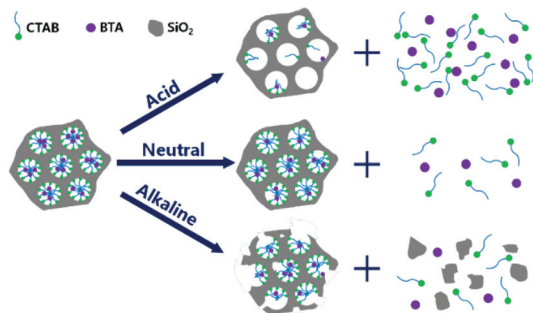




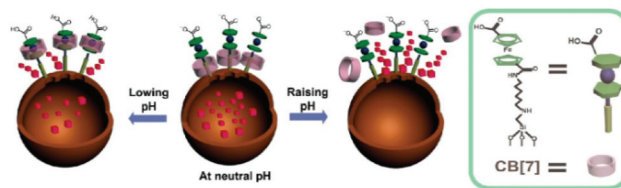
A pH controlled release of 8-HQ from MSN was designed by Shchukina *et al.*<sup>106</sup> and Shi *et al.*,<sup>68</sup> which demonstrated the stability of these nanocontainers at neutral and slightly acid or basic pH and the corrosion inhibitor release in stronger acid and alkaline environment. A similar behaviour was proposed by Kermannezhad *et al.*,<sup>52</sup> who reported an almost complete release of MBA at very low and high pH (over 80%), an intermediate release at slightly acid or basic pH (around 60%) and a very low release at neutral pH (after 50 h, 40% of MBA was released).

Other alkaline pH-responsive nanocontainers were developed exploiting the instability of the bond N-Fe in basic conditions with EBT as corrosion inhibitor,<sup>55</sup> the trigger mechanism of pillararenes to activate the HMAP release<sup>133</sup> and PSS/PEI layers polyelectrolyte opening system which allows PAA release<sup>144</sup> and BYS.<sup>143</sup> Alkaline ambient sensitive nanoparticles were also showed in another work, where MSN loaded with BTA and covered with PSS/PEI polyelectrolyte layers were developed.<sup>142</sup>

BTA is widely exploited in pH-responsive nanocontainers applications,<sup>105,119,140–142,145,152</sup> due to the repulsive electrical force induced by moving from neutral pH to acid or basic pH.<sup>105</sup> Therefore, BTA release is encouraged both in acid and in alkaline solutions, as reported by Borisova *et al.*,<sup>105</sup> who simply loaded BTA in MSN and observed the corrosion inhibitor release rate, and Grigoriev *et al.*,<sup>145</sup> who tested some pH-responsive polyelectrolyte layers, made by PEI, BYS and poly(allylamine hydrochloride) (PAH) or poly(diallyldimethylammonium chloride) (PDADMAC) and molybdate. BTA was also released from MSN capped with TA-Fe complex by Qian *et al.*,<sup>152</sup> who revealed an increased corrosion inhibitor release with the acidification of the ambient, and from Xu *et al.*,<sup>119</sup> who realised a one-step synthesis and loading of MSN-BTA-CTAB nanoparticles (Fig. 9). In this paper, the authors observed that the CTAB presence in the MSN pores promotes the release in acid conditions, while, increasing the pH until basic values, the release rate was considerably decreased. CTAB did not allow the release in alkaline media and the release substantially started when the MSN were etched by the exposition to OH<sup>-</sup> ions.



**Fig. 9** Release mechanism from MSN-BTA-CTAB: release rate decreases with the increase of pH. Reproduced under permission from ref. 119.



**Fig. 10** Caffeine release from MSN functionalized with pseudorotaxane nanovalve. Adapted with permission from ref. 129. Copyright 2013 American Chemical Society.

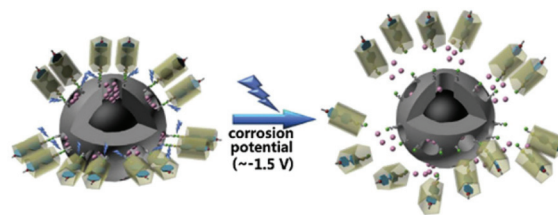
Castaldo *et al.*<sup>141</sup> and Zheng *et al.*<sup>140</sup> studied the kinetic release of BTA complexed with copper ions in acid conditions revealing, also in this case, the increasing in BTA release with the acidification. Wen *et al.*<sup>149</sup> observed an encouraged alkaline release of BTA loaded in PEI covered MSN.

With the CB[7], HDA and FCDCA pseudorotaxane nanovalve installed on the MSN by Fu *et al.*,<sup>129</sup> encapsulated caffeine exploited the pH-responsive system following the mechanism schematized in Fig. 10: at neutral pH the CB[7] acted as gatekeepers, while lowering or raising the pH the interactions between CB[7], HDA and FCDCA promoted the caffeine release. In particular, corrosion inhibitor release is highly encouraged toward very low or high pH.

Chen *et al.* studied the release of BTA from surface modified MSN with CB[6] and cyclodextrin based nanovalves, developing different systems with tailored BTA release in both acid and alkaline conditions.<sup>130,131</sup>

### Other triggering mechanisms

**Electric potential variation triggered mechanisms.** A supramolecular switch made of pillararenes onto Fe<sub>3</sub>O<sub>4</sub> modified MSN encapsulating 8-HQ was developed by Ding *et al.*<sup>134</sup> With the obtained nanocarriers they covered a magnesium alloy substrate and demonstrated that this supramolecular structure is sensitive to electric potential variations. Indeed, corrosion processes involve electric potential variations and, tuning the detachment of the pillararenes switch with the electric potential, the authors induced the corrosion inhibitor release from the MSN (see Fig. 11). Similar results were conducted by Wang *et al.*,<sup>136</sup> who developed redox-triggered nanoparticles activated by ferrocene moieties, using  $\beta$ -CD as capping system and CA as corrosion inhibitor onto an aluminium alloy substrate.



**Fig. 11** Pillararenes supramolecular switches activation through corrosion potential variation. Reprinted with permission from ref. 134. Copyright 2017 American Chemical Society.



**Light-responsive switches.** An interesting approach for inhibitors release is based on light-responsive smart nano-carriers. In contrast to pH-sensitive systems, light stimulation is independent from the corrosion process, and therefore can be activated or deactivated on-demand.<sup>5,142</sup> The corrosion inhibitors release is induced by UV radiation in the smart nanocontainers developed by Chen *et al.*<sup>5</sup> They exploited the *cis/trans* isomerization of azobenzene, which was grafted into HMSN loaded with BTA: in *cis* configuration, azobenzene allows the BTA release, while, in *trans* configuration, azobenzene closes the pores. They also showed how pH variation did not substantially modify BTA release amount and rate, while the UV irradiation allows the complete BTA release, which is inhibited if the nanocontainers are exposed to visible light. In an already mentioned Skorb's work,<sup>142</sup> related to BTA release from MSN in alkaline media, they observed corrosion inhibitor release under IR laser irradiation, incorporating silver nanoparticles into polyelectrolyte layers outside the nanoparticles, in order to install light absorption dots (silver has very high surface resonance plasmon band). In this way, the BTA release amount was considerable higher with respect to the release obtained by simply exposing the nanocontainers to an alkaline solution.

**Ion concentration triggers.** Ion concentration change is also a trigger for corrosion inhibitor release. Maia *et al.*<sup>51,53</sup> showed an increased release of loaded molecules from MSN into an aqueous solution with increasing the sodium chloride concentration, due to the interaction between corrosion inhibitor and NaCl, which promotes the formation of sodium salts with higher solubility than pure corrosion inhibitor. Zheng *et al.*<sup>140</sup> observed that the BTA-Cu complex is responsive to sulphide ions concentration variations, and it dissolves in response to the Na<sub>2</sub>S concentration increase in an aqueous solution, therefore promoting the BTA release. Ding *et al.*<sup>133</sup> realised a pillar-arenes nanovalve on HMAP loaded MSN which reacts with magnesium ions, creating a complex that interferes with the capping of the nanoparticles, inducing the corrosion inhibitor release.

**Temperature influence on corrosion inhibitor release.** As in light-dependant smart nanocarriers, temperature is an external parameter, not directly correlated to corrosion phenomena. However, several works include temperature-responsive silica nanocontainers.<sup>153,154</sup> This trigger is not much investigated for corrosion applications and is usually connected to light irradiation.<sup>142</sup> However, temperature can influence corrosion inhibitor release, as showed by Kermannezhad *et al.*,<sup>52</sup> who underlined the capability to modify the release of MBA from pH-dependant MSN in response to a temperature variation of the surrounding environment, observing an increase in corrosion inhibitor release with the temperature increase.

**Redox reactions release systems.** Wang *et al.*<sup>136</sup> developed a supramolecular switch made by ferrocene and  $\beta$ -CDs sensitive to redox stimuli, activated by cerium(IV) salts (ceric ammonium nitrate, H<sub>8</sub>N<sub>8</sub>CeO<sub>18</sub>) which were able to react with ferrocene, opening the nanovalve and inducing the CA release. They

**Table 5** Triggering mechanisms for corrosion inhibitors release

Release mechanism trigger	Ref.
pH	51, 52, 54, 55, 68, 69, 104, 105, 106, 108, 113, 119, 129, 130, 131, 133, 140, 141, 142, 143, 144, 145, 147, 149 and 152
Electrical potential	134 and 136
Light	5 and 142
Ion concentration	51, 53, 133 and 140
Temperature	52,142,153 and 154
Redox reaction	128 and 136

observed an increase in CA release, increasing cerium concentration. Moreover, after redox reaction, cerium salts were reduced to cerium(III) salts, an inorganic corrosion inhibitor, generating a double anti-corrosive effect. In Sun's work,<sup>128</sup> the redox stimulus was activated by dithiothreitol (DTT) with ZnO quantum dots (QDs), which acted as nanovalves outside the nanoparticles. They observed that the MBT amount and kinetics of release are promoted by the increase of DTT concentration. In Table 5 the triggering mechanisms above reported are summarized.

## MSN in smart anticorrosion coatings

### Anticorrosive solutions: from passive barriers to smart nanostructured coatings

Corrosion is a phenomenon whose related costs have been estimated as about 3–4% of the gross domestic production in Western Countries. On this basis, the global cost of corrosion can then be valued about USD 2.5 trillion per year. Using available mitigation strategies, a possible cost saving of 15–35% has been estimated, corresponding to USD 375–875 billion on a global basis.<sup>155</sup> In this frame, protective polymer coatings are considered the main prevention and mitigation strategy to corrosion.<sup>156</sup>

Most of the commercially available organic coatings exploit their protective function acting as a barrier layer towards pollutants. The history of these types of passive protective coatings is very ancient.<sup>157</sup> One of the first examples of coatings based on organic materials was documented in 77 AD by Pliny the Elder, who reported the use of a mixture containing tar to protect iron against rust.<sup>158</sup>

Adding additives to a polymer phase to impart functional properties to the coatings is a relatively new concept. A few years ago, additives were reported as possibly able to impart functional properties to the coatings in a number of ways that were not always proven beyond doubt.<sup>159</sup> Instead, in the last years, nanotechnology applications in coatings have shown a remarkable growth. This was a result of the increased availability of nanoscale materials, such as various types of nanoparticles, as well as the development of interesting experimental approaches able to realize organic-inorganic hybrid coatings by exploiting the concept of preparation of nanoparticles by *in situ* sol-gel<sup>160,161</sup> and the advancements in pro-



cesses and characterization methods, that can control and validate the coating structure at the nanoscale.<sup>162–164</sup>

The use of nanoadditives in polymer coatings has been proposed in the years with objectives characterized by an even higher complexity. First, nanostructured additives have been used to improve the mechanical, thermomechanical and barrier properties of the coatings. For mechanical and thermomechanical properties, with a typical approach used in nanocomposites aimed at reducing the polymer chain mobility and increasing the elastic modulus of the polymer matrix, 0D,<sup>165</sup> 1D<sup>166,167</sup> and 2D<sup>168</sup> nanostructured additives have been widely used. For barrier properties, the most relevant effects were obtained using 2D nanoadditives, such as lamellar clay,<sup>169,170</sup> or graphene derivatives.<sup>171,172</sup> Then, different types of nanoparticles were used to impart peculiar physical–chemical properties, such as hydrophobicity,<sup>173</sup> UV blocking<sup>174</sup> and antibacterial properties.<sup>175,176</sup> In most cases the effectiveness of the smart coating was optimized by improving the nanoparticles dispersion into the coating and the nanoparticle/coating interfacial adhesion, key factors to obtain high performance nanocomposite materials.<sup>177–179</sup> Also for MSN, relevant papers demonstrated that homogeneously distributed nanoparticles reduce the defects of the coatings, prolonging their physical barrier efficacy.<sup>129,133</sup> For instance, Xie *et al.*<sup>124</sup> showed that the addition of nanoparticles improved corrosion resistance because of the superior morphological features of the resulting coating, which was smoother and more homogeneous.

More recently a different strategy was exploited to maximize the properties of nanostructured coatings. In this new research line, the effort was not aimed at promoting the nanoparticle dispersion but their assembly in complex architectures.<sup>180–182</sup>

In parallel, in the last decade, in the coating sector, nanoparticles started to be considered not only as a way to tailor the properties of the matrices in which they were embedded through their optical, chemical and morphological features or their self-assembly capability. Indeed, the cargo capability of selected nanostructured materials found an always increasing interest for coating application. The idea of including within the coating a nanomaterial able to transport active agents and release them under stimuli, *i.e.* a nanocarrier, was very exciting and paved the way to the development of a new class of highly smart coating systems with incommensurable improved protection effectiveness and durability with respect to the passive coating systems.

In this frame, in the last years the research on the design of smart coatings containing various type on nanocarriers has undergone a significant increase. Nanocarriers are used in coatings for different purposes. First, they must release specific substances *in situ*, *i.e.* very close to the place where these active agents exploit their function. Thus, as already shown in the previous sections, the design of the nanocontainer plays a fundamental role to tailor the control of the active agent release in different conditions or under specific external stimuli. Moreover, they can protect the active agent from degradation, thus ensuring a long-lasting efficiency.<sup>32,141</sup> Moreover, single nanocarriers or mixtures of different nano-

carriers can exploit in coating multifunctional properties because they can show improved mechanical, thermomechanical and barrier properties and at the same time they can respond to several stimuli, protecting the substrate from chemical as well as physical damage *via* on-demand release of corrosion-inhibitors.<sup>183,184</sup>

Amongst different nanocarriers used in coating applications, recently MSN based coating are showing an even growing scientific interest. These advanced coating exploit most of the active agents' release mechanisms described and discussed in the previous sections.

Anticorrosive coatings may be based on alkyd resins,<sup>5,56,119,152</sup> epoxy resins,<sup>59–61,108,113,115,122,149,150,185</sup> eventually modified with amino hardener<sup>51</sup> or mixed with polyamide<sup>68</sup> or silicone,<sup>69</sup> polyesters,<sup>106,123,140</sup> acrylic resins,<sup>141</sup> and polypyrrole.<sup>54,58</sup> Sol–gel coatings are also investigated, obtained by TEOS and derivatives, such as (3-glycidioxypropyl)trimethoxysilane (GPTMS),<sup>55,129,134,144</sup> eventually functionalized with fluorine-containing monomers,<sup>133</sup> methacryloxypropyltrimethoxysilane (MAPTS),<sup>147,148</sup> or hybrid silane/zirconate coatings.<sup>104,105,114,131,136,142,143,145</sup>

Thus, the validation and characterization of these coating systems becomes crucial to critically evaluate the potential beneficial effects of mesoporous silica nanocarriers for anticorrosion applications and thus to identify the most promising perspectives in this still highly scattered research topic.

### Validation and optimization of MSN based anticorrosion coatings

The validation of the performances of the anticorrosive systems is usually carried out on metallic substrates covered by smart coatings, *i.e.* coatings in which the functional MSN are embedded, or on model systems consisting of electrolyte solutions in which the functional MSN containing the active agents are dispersed.

In the case of smart coatings, the substrates are exposed to corrosive environment in controlled conditions in order to evaluate the evolution of specific physical parameters related to corrosion phenomena. Typical tests are conducted comparing the anticorrosive efficiency of the smart coatings with coatings containing the freely dispersed corrosion inhibitor, plain coatings and eventually uncoated samples. Although smart nanocontainers are studied to be theoretically able to prevent corrosion on each kind of metallic substrate, researchers usually projected their systems for specific applications, identifying a metal and characterizing the anticorrosive performances of their smart nanocarriers on specific substrates. Chosen substrates are typically those applied in fields such as aerospace, construction engineering and cultural heritage: several works included tests onto aluminium alloys,<sup>5,51,68,105,113,114,118,120,129,131,136,142,143,145,185</sup> steel,<sup>52,54,55,57–61,69,104,106,108,122,123,140,144,147,148,149,150,152</sup> copper alloys<sup>52,62,119,141</sup> and magnesium alloys<sup>56,115,124,133,134</sup> (Table 6).

As summarized in Table 6, the corrosion protection efficiency is evaluated by various analytical techniques, including electrochemical, morphological and spectroscopic tech-



Table 6 Corrosion evaluation techniques

Technique	Analytical technique	Substrate	Ref.
Electrochemical techniques	Electrochemical impedance spectroscopy (EIS)	Al alloy	51, 68, 113, 114, 118, 129, 131, 136 and 185
		Cu alloy	52 and 62
		Mg alloy	56, 115, 124, 133 and 134
		Steel	52, 55, 57, 58, 59, 60, 61, 69, 104, 108, 122, 123, 140, 144, 149, 150 and 152
		Steel	144 and 148
	Scanning vibrating electrode technique (SVET)	Al alloy	5, 68, 105, 113, 114, 129, 136, 142, 143, 145 and 185
		Cu alloy	119
		Mg alloy	133 and 134
		Steel	123, 140 and 144
	Localized electrochemical impedance spectroscopy (LEIS)	Steel	144 and 148
		Steel	144 and 148
	Potentiodynamic polarization (PDP)	Mg alloy	124 and 133
		Steel	52, 57, 69, 108 and 150
	Scanning Kelvin probe force microscopy (SKP)	Cu alloy	62
		Mg alloy	134
		Steel	147 and 148
		Steel	147 and 148
Salt spray test	Al alloy	68	
	Steel	106	
Hydrogen evolution measurement	Mg alloy	124	
	Al alloy	113	
Machy test	Al alloy	113	
	Steel	60	
Morphological analyses	Electrochemical noise measurement (EN)	Steel	60
		Al alloy	5, 51, 56, 68, 105, 120 and 129
		Cu alloy	141
		Mg alloy	134
	Optical microscopy	Steel	60, 140, 149 and 152
		Steel	104
	Surface profiler	Mg alloy	124
		Steel	147 and 148
	Three dimensional optical profilometer	Mg alloy	124
		Steel	147 and 148
	Scanning electron microscopy (SEM)	Al alloy	5, 51, 105, 131, 136, 143 and 145
		Cu alloy	119 and 141
		Mg alloy	56, 115, 124, 133 and 134
		Steel	54, 55, 58, 59, 60, 61, 69, 104, 106, 108, 123 and 152
	Focused ion beam (FIB)	Al alloy	136
		Mg alloy	134
	Atomic force microscopy (AFM)	Al alloy	5, 105, 129, 131, 142, 143 and 145
Cu alloy		119	
Mg alloy		133 and 134	
Steel		55	
Spectroscopic analyses	Energy dispersive X-ray analysis (EDX)	Al alloy	5, 68, 131 and 136
		Cu alloy	141
		Mg alloy	56, 124 and 134
		Steel	55, 60, 61, 69 and 104
	Fourier transform infrared spectroscopy (FTIR)	Mg alloy	115
		Steel	54, 55 and 58
	X-ray diffraction (XRD)	Mg alloy	56
		Steel	54 and 58
	X-ray photoelectron spectroscopy (XPS)	Mg alloy	124 and 133
		Steel	59
Infrared reflection absorption spectroscopy (IRRAS)	Al alloy	143	
	Al alloy	143	

niques. Besides the corrosion progression, electrochemical techniques allow to determinate the efficacy of nanoparticles distribution onto the metal substrate, collecting electrical parameters (such as impedance in EIS or anodic and cathodic current in SVET), while morphological and spectroscopic analyses evaluate also the formation of protective compounds onto the metal surface and the self-healing properties of the coating. In fact, some authors evaluated the efficacy of a specific functionalization or the study of compounds produced during the corrosion process. Yeganeh *et al.*<sup>61</sup> confirmed by XRD the formation of protective compounds such as MgF<sub>2</sub>, induced by fluoride ions release onto a magnesium substrate, in contrast to the formation of MgO in absence of corrosion

inhibitors,<sup>56</sup> and Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> and other molybdenum oxides, due to Mo ions release which reacted with Fe of the steel surface.<sup>59</sup> A similar result was obtained by Xie *et al.*,<sup>124</sup> which observed by XPS the presence of magnesium oxides MgO and MgOH on a magnesium substrate in absence of the corrosion inhibitors smart nanocarriers and the formation of MgF<sub>2</sub>, which improves corrosion resistance, in presence of the smart MSN.

Observing by SEM coatings containing embedded organic inhibitors, the amount of corrosive products after short time is generally low,<sup>105,114,133</sup> in contrast to coatings doped with inorganic active molecules, which quickly react with the metal surface.<sup>54,56,59,136</sup> Alipour *et al.*<sup>57</sup> motivated the MPTMS



functionalization of MSN asserting that the functionalization improves the barrier properties of the coating, reducing its porosity, and enhances the adhesion to the metal substrate, increasing the coating hydrophobicity. Moreover, an hydrophobic functionalization can directly improve the barrier properties of the coatings, thus reducing the corrosion rate of the treated substrate.<sup>133</sup>

Hollamby *et al.*<sup>123</sup> improved the MSN dispersion in a polyester-based coating by functionalizing the nanoparticles with OTES. Moreover, they underlined that free dispersed BTA in the polyester coating is not effective in preventing corrosion phenomena due to the BTA interactions with the polymer network during the curing step, while the use of corrosion inhibitors nanocarriers, such as MSN, inhibits the BTA interaction with the polymer network and enables an improved corrosion protection. MSN act as smart reservoir of inhibitors, and they do not affect adhesion and barrier properties of the coating.

Several works report that at early times of exposure to corrosive environments the use of MSN as smart nanocarriers may not give a substantial advantage with respect to the use of free inhibitor, owing to slow inhibitor release.<sup>5,51,124,129,134,136</sup> Nevertheless, MSN show significant advantage in corrosion protection at long-time observation, providing higher durability of the active coating. Moreover, MSN also act as a shield from UV radiation for the loaded molecules. For example, Castaldo *et al.*<sup>141</sup> demonstrated that the use of MSN as smart nanocarriers of corrosion inhibitors allows to prolong the durability of metal protective coatings, protecting the corrosion inhibitors from possible photodegradation.

Moreover, corrosion resistance of coatings containing MSN can be tailored by optimizing the quantity and size of embedded MSN as well as the amount of encapsulated inhibitor and the evaluation of the coating barrier properties can be independent from the corrosion inhibition. The optimal amount of MSN to be embedded into coatings depends on the specific tested system but, generally, electrochemical measurements show that 1–4 wt% are the maximum amount of nanocontainers able to provide corrosion inhibition.<sup>108,115</sup>

Borisova *et al.*<sup>113</sup> explored the corrosion resistance behaviour of MBT loaded MSN tuning the MBT loading and the nanoparticles dimensions. Fixing the anticorrosion inhibitor loading at about 20% by weight within the nanocarriers, they considering two sizes (80 nm and 700 nm diameter), and they found that for both particle size also very low MSN amounts, such as 0.04 wt%, are able to induce an increased corrosion resistance of the coatings. Moreover, they also evaluated 1.7 wt% as an upper limit composition for the bigger MSN (700 nm). Above this amount, barrier properties of the coating dramatically fail, with loss of the coating durability due to an easy penetration of corrosive media that easily reach the metal substrate. This phenomenon is due to the increased presence of defects into the coating. The compromise between good corrosion inhibition and barrier properties was found at 0.7 wt% of MSN with 80 nm diameter.<sup>185</sup> Moreover, they also proposed the application of two overlapped protective coatings on metal

substrates, embedding MSN only in one of the coatings and founding that the selective localization of MSN in the coating closer to the metal surface improves the protection from corrosion, while the best barrier properties were observed when MSN were included in the external coating. Finally, embedding MSN in the external coating layer at 0.5–0.7 wt% loading amount provided the optimal result in terms of corrosion inhibition/barrier properties balance.<sup>114</sup>

## Conclusions and perspectives

As shown in the previous sections, MSN find large application potentialities for the realization of effective anticorrosive coatings. Within this broad topic, in this review 3 main research subtopics have been identified and discussed:

- (a) The synthesis of MSN with tailored porosity and structure;
- (b) The design and development of corrosion inhibitor gate/release mechanisms;
- (c) The use of MSN in smart anticorrosive coatings and the validation of the coating performances.

As concerning the synthesis, MSN with tailored size and size distribution and with controlled pore size and geometry are currently widely investigated. Nevertheless, based on the analysis of the literature, further research is still needed with the following specific objectives:

- (a1) To optimize the synthesis of MSN, developing sustainable, high yield/high throughput processes;
- (a2) To optimize one-step synthesis/functionalization/loading processes that will reduce the production costs of MSN, a limiting factor for several applications;
- (a3) To set up viable procedures to realize MSN with maximized cargo capability of active agents, such as MSN with an inner reservoir and a mesoporous shell (hollow MSN), with optimized size and volume ratio between the core and the shell.

For the development of the loading/gate/release mechanisms, research performed so far have been focused on the design and test of gating systems with different degrees of complexity, including physical adsorption of the active agents in the mesopores, covalent grafting of the active agents, formation of stable chelating complexes of the active agents, physical capping of the pores with various chemical species (nanovalves, polyelectrolytes). Together with a specific gating system, each research has usually proposed a corresponding stimuli-responsive mechanism able to promote the on-demand release of corrosion inhibitors in response to the variation of physical parameters. The most investigated triggers to promote the release of anticorrosion agents are changes of pH, ions concentration, electrical potential and light irradiation. Due to the specificity of the proposed gating/release mechanisms, a comparison between the different approached proposed is very hard. Each approach has peculiarities that make it highly effective in response to a specific stimulus. Very interesting are the gating/release mechanisms based on pH respon-



sive chelating complexes and on layer-by-layer polyelectrolytes. In this frame, the most interesting research perspectives should address to:

(b1) Maximize the loading efficiency of active agents, still limited also due to the partial release of the actives during the successive application of the gating system; in fact, often, more than 70% of the pore volume of the particles is unexploited in the available research works, thus underestimating the cargo potentiality and then the effectiveness of MSN;

(b2) Develop new and even more effective gating/release mechanisms, properly designed for new class of active agents, in particular bio-based and sustainable anticorrosion agents;

(b3) Develop gating/release mechanisms properly designed for specific target applications (protection of metals, alloys and concretes in buildings and marine environments, transportation and aeronautics, cultural heritage).

Finally, for the embedding of MSN in coatings to realize smart anticorrosion systems, current researches are mainly focused on the optimization of the relative amount of MSN and their effective dispersion within the coatings and on the validation of the smart coatings through different methods. In this frame, the most promising research trends and perspectives are:

(c1) The optimization of the gating/release mechanism and the release kinetics of the active agents within the coating, as the release mechanisms and kinetics are usually optimized on nanoparticles dispersed in model systems (mainly water dispersions);

(c2) The promotion of the self-assembly of the nanoparticles in specific morphologies, to optimize the release of the active agents in the exact place in which they are needed;

(c3) The realization of smart coatings embedding different MSN loaded with different anticorrosion agents, in this way reproducing the approach adopted in commercial anticorrosion products, that usually contain mixtures of different of active agents;

(c4) The optimization of the interfacial adhesion between the particles and the matrix to guarantee high mechanical and barrier properties of the coatings that, synergistically combined with the stimuli-responsive release of the active agents, should be able to ensure the best corrosion protection;

(c5) The development of highly effective multifunctional smart coatings in which, in addition to the passive barrier and the stimuli-responsive release of the active agents, the coatings would be able to entrap or deactivate the corrosive agents before they enter in contact with the substrate to be protected;

(c6) The development of reversible smart coatings, with self-healing properties based on reversible mechanisms of formation/opening of dynamic bonds;

(c7) The development of smart environmentally sustainable and safe-by-design smart coatings, based on renewable materials, and realized following the main paradigms of the circular economy.

Thus, this review demonstrates that there is here certainly plenty of scope for improvement in the field of MSN and their

use in smart anticorrosive coatings. Following the identified research trends and perspectives, or developing new breakthrough approaches to exploit the highly interesting properties of MSN, can pave the way to the development of a new class of smart anticorrosive coatings with extraordinarily superior properties with respect to current commercial products used in different sectors (cultural heritage, civil and industrial infrastructures, transportations and airspace), thus contributing to preserve our past history and culture and to protect our future.

## Conflicts of interest

There are no conflicts to declare.

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