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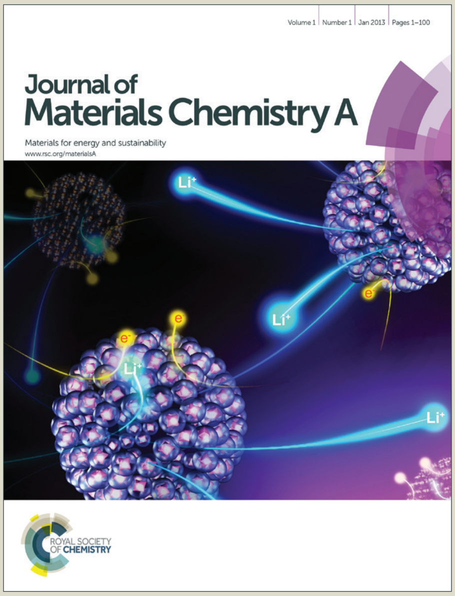

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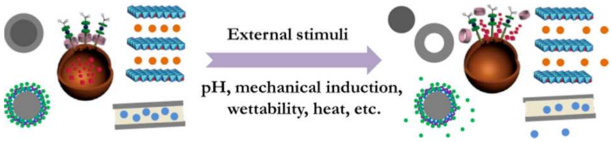

Smart self-healing micro/nanocontainers by releasing active compounds to heal cracks in the coating in response to external stimuli were reviewed.

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Review

Advanced Micro/Nanocapsules for Self-Healing Smart Anticorrosion Coatings

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Smart self-healing coatings for corrosion protection of metallic substrates (steel, magnesium, and aluminium, and their alloys) have attracted tremendous interest due to their capability to prevent cracks propagation in the protective coatings by releasing active agents from micro/nanocapsules, that is, micro/ nano particles consisting of a coating layer or a shell (micro/nanocontainer) and core material (solids, droplet of liquid or gases), in a controllable manner. This paper aims to give a concise review on the most recent advances in preparing micro/nanocapsules based on different types of micro/nanocontainers, i.e., organic polymer coatings, inorganic clays, mesoporous silica nanoparticles, and polyelectrolyte multilayers, etc. for smart coatings with self-healing properties. The state-of-the-art design and preparation of micro/nanocapsules are highlighted with detailed examples.

1. Introduction

Metals including steel, magnesium, aluminum, and their alloys are widely used in industrial and engineering structures for their high strength and ductility.[1,2] However, substantial financial losses have been caused by metal corrosion which is defined as "physicochemical interaction between a metal and its environment, which results in changes in the properties of metal and which may often lead to impairment of the function of metal, the environment, or the technical system of which these form a part" (ISO 8044-1986). It's estimated that global annual cost of corrosion amounts to around 4.2% of the gross national products (approximately \$100 billion in USA and around €200 billion in Europe).[3] Therefore, corrosion protection has become an issue of prime importance to minimize the economic losses. Varieties of strategies have been developed to slow down the kinetics and/or altering the corrosion mechanism. For example, conventional methods such as cathodic protection by employing a sacrificial anode can decrease the oxidation rate whereas anodic protection through a protective passive, i.e., oxide layer on the metal surface will be able to minimize the reduction rate.[4]

Application of coatings is the most common strategy to protect metals from corrosion.[5] Generally, the coating consists of several layers, of which the most important ones are pretreatment layer, primer and topcoat.[6,7] The pretreatment

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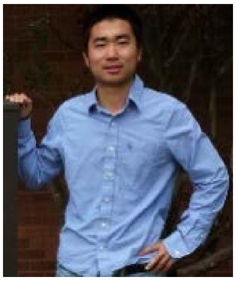

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layer plays an essential role to increase the adhesion between the metallic substrate and the primer. The primer layer is mainly used to improve the corrosion protection of the metal substrate. Chromate based conversion coatings (corrosion resistant films converted from the metal substrate surface by a chemical or electro-chemical process)[8] have demonstrated superior anticorrosive effectiveness in aeronautics.[9,10] However, the great concern about the carcinogenic Cr(VI) on the environment has promoted the development of alternative environmentally friendly systems.[11] So far, varieties of materials have been explored, such as anodized coatings,[12] layered double hydroxide (LDH) inorganic conversion coatings,[13] and hybrid organic-inorganic sol-gel films.[14,15] An alternative of "green" chitosan, a linear polysaccharide, is also reported as a potential candidate of pretreatment due to its excellent adhesion to metallic surfaces and to many organic polymers.[16,17] In the case of primers, conventional organic coatings or paints, including polyurethane,[18] epoxy,[19] alkyd primers,[20] and polyvinyl butyral[21] are usually utilized considering their low cost, easy application, and aesthetic functionality. Recently, intrinsically conductive polymers (ICPs) including polyaniline (PANI), polypyrrole (PPy), polythiophene and their derivatives, have become a topic of interest for corrosion prevention of metals.[1,22] These ICPs can be used either in their pure form or composite forms, blended with conventional paints, or additives to modify a conventional paint. Specially, renewable resources like coconut oil based ICP composite coatings have attracted increasing attention due to growing concerns about environment protection and sustainability.[23,24] A proper topcoat is necessary that works as sealing agents to prevent the penetration of anions. The topcoat can be epoxy or polyurethance materials with low water vapor permeability.[25,26]

It is generally accepted that the coatings provide a passive barrier blocking the passage of oxygen and water, and increase the resistance of ion movement at the metal/electrolyte interface.[27] However, the coatings are susceptible to cracks formed deep within the structure because of changes in the mechanical properties of the coatings during their service life. The cracks propagate and expose the substrate to atmospheric moisture and oxygen, finally leading to the failure of the coatings. The detection of initial micron cracks is difficult and the reparation is almost impossible. Therefore, the design of smart coatings with self-healing properties, the concept of which is pretty new, turns out to be a promising route to address the above challenge.[28,29] A smart coating with self-healing properties is one that changes its properties in response to an environmental stimuli such as heat, light irradiation, mechanical induction, pH, wettability, temperature, aggressive corrosive ions, and etc., and heal damages without any external intervention.[30–34] The self-reparation capability of smart coatings without manual intervention prolongs service life of the coatings while significantly reduces the maintenance cost. Some excellent work has been carried out in the polymeric system by Yang's group in Nanyang Technological University, Singapore. The concept of self-healing has also been successfully demonstrated in the ceramic matrix using MAX-phase ceramics as the healing agent, where M is the transition metal, A is an A group element (mostly IIIA and IVA, like Al

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and Si), and X is C and/or N, by Van der Zwaag's group in TU Delft University of Technology, Netherland. The self-healing properties arise from the formation of a stable, well-ahering oxide with relative high volume expansion and having mechanical properties close to those of the matrix.[35,36]

Two strategies have been reported for designing self-healing smart coatings, i.e., direct doping of coatings with inhibitors and encapsulation of active materials (polymerisable agents, inhibitors, et al.) in the micro/nanocontainers or reservoirs that are distributed uniformly in the coating.[37] For the direct doping technique, there are problems of early leakage of the inhibitor and undesirable interactions between the matrix and the inhibitors, which disrupt the barrier properties of the coatings. In contrast, to encapsulate active materials inside micro/nanocontainers can overcome the aforementioned limitations of direct doping. Generally speaking, micro/nanocapsules are particles (ranging from several nm to a few mm) containing a core (solid, droplet of liquid, or gases) surrounded by a coating layer or a shell (micro/nanocontainer).[38] The design of micro/nanocontainers plays an important role in determining the performances of protective coatings. The ideal micro/nanocontainers are proposed to be featured with (1) chemical and mechanical stability, (2) compatibility with the coating matrix, (3) sufficient loading capacity, (4) impermeable shell wall to prevent leakage of active substance, (5) the ability to sense corrosion onset, and (6) release of active substance on demand.

Although smart coatings have been regularly reviewed,[2,5,39–44] a review dedicated to the latest trend of the micro/nanocapsules is necessary. Therefore, the paper aims to give a complete yet concise review on the state-of-the-art development of micro/nanocapsules based on different types of micro/nanocontainers including organic polymers, inorganic clays, mesoporous silica nanoparticles, and polyelectrolyte multilayers. Other micro/nanocapsules using innovative micro/nanocontainers will be discussed as well.

2. Self-healing smart coatings for anticorrosion

As aforementioned, self-healing smart coatings are able to heal the cracks if the local environment undergoes changes or the active surface is affected by the outer impact. To achieve this functionality, micro/nanocontainers are usually loaded with polymerizable agents or inhibitors, and are then dispersed in the coating matrix. Materials with porous, hollow, or layer structures and their assemblies are often preferred as micro/nano containers. The core material, or active material, can be either polymerizable monomers or inhibitors. Dicyclopentadiene[45–47] and epoxy[48,49] are two common polymerizable components in the former case. The disadvantage of this approach is the requirement of high monomers content being stored in relatively large polymeric capsules, which is quite challenging for the capsules to be evenly dispersed within liquid paint.[50]

Micro/nanocontainers loaded with inhibitors for self-healing coatings are another promising choice. Inhibitors containing nitrogen organics such as the azole groups, amines, and amino acids are mostly used. The corrosion protection capability is achieved via the formation of isolative films formed between metal ions and nitrogen heterocycles.[31]

To study the surface morphology, protection mechanism, and healing rate of self-healing coatings, electrochemical techniques are most commonly used tools. Specially, spatially-resolved electrochemical tools including scanning vibrating electrode technique (SVET), localized electrochemical impedance spectroscopy (LEIS), and scanning ion-selective electrode technique (SIET) have been proved to be the most powerful and useful measurements for evaluating corrosion protection ability of the self-healing coatings.[51–53] Other electrochemical techniques such as open circuit potential (OCP), potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS), odd random phase multisine EIS (ORP-EIS), scanning electrochemical microscope (SECM), electrochemical noise analysis (ENA), and electron probe microanalysis (EPMA) have also been reported for studying anticorrosion protection behavior of self-healing coatings.[54–56] Fayyad et al. suggested linear polarization resistance (LPR), cyclic potentiodynamic polarization (CPDP), scanning kelvin probe (SKP), and hydrogen evolution reaction tests (HERT) as possible tools for self-healing coatings study.[20] Other non-electrochemical methods include salt spray test,[57] rheological and spectroscopic study, et al.[58]

2.1 Polymer coatings based micro/nanocapsules

Polymeric micro/nanocontainers are one type of the most important carriers for core materials in self-healing smart coating applications. There are several methods to synthesize the polymeric micro/nanocapsules including interfacial polymerization, coacervation, extrusion, and sol–gel methods. The most common one is the in situ polymerization-oil in water (O/W) emulsion for the encapsulation of core materials.[59] The advantages lie in its convenience and easy preparation. Briefly, the hydrophilic shell material monomers are dissolved in the continuous aqueous phase. The catalyst is added and the heating is applied in the presence of all the shell-forming reactants, and the polymerization starts. The polymerization process propagates on the core material droplets surface and yields a solid polymeric shell.

Utilization of polyurea-formaldehyde (PUF) microcontainers loaded with polymerisable agents is one of the first strategies proposed to develop self-healing coatings with reparation functionalities.[60] Pioneering work has been done by Scott R. White's group in University of Illinois. As illustrated by Fig. 1, the self-healing process was triggered by a crack-induced rupture of the embedded capsules. The polymerization process based on ring open metathesis polymerization (ROMP) of released core material dicyclopentadiene (DCPD) from torn capsules requires Grubbs' catalyst (a series of transition metal carbene complexes used as catalysts for olefin metathesis)[61] that must be dispersed into the coating matrix.

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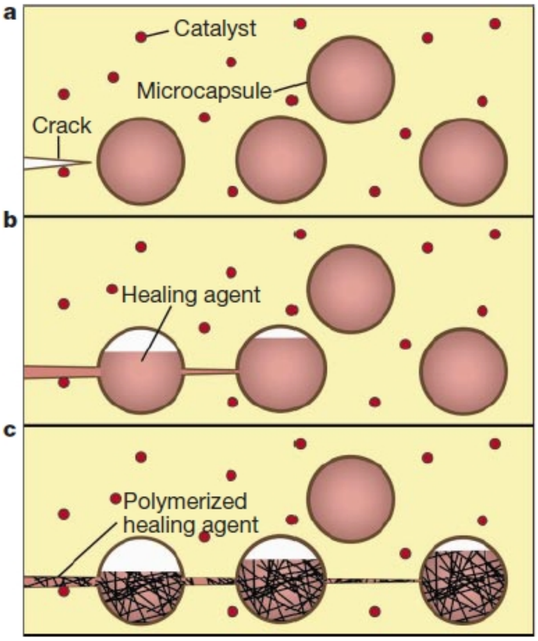

Fig. 1 Illustration of autonomic healing concept. Microcapsules loaded with the polymerizable healing agent are dispersed in a structural composite matrix containing the corresponding catalyst. (a) Cracks form in the matrix due to the damage; (b) the cracks rupture the microcapsules and the healing agent is released into the crack plane through capillary action; (c) the healing agent contacts the catalyst, inducing polymerization to bond the crack faces closed. Reprinted by permission from Macmillan Publishers Ltd: [Nature] (Ref. 60), copyright (2001)

So far, PUF remains a popular polymer microcontainer for self-healing smart coatings. The preparation of microcapsules can be one- or two- step processes.[62] In the former, polymerization of urea with formaldehyde starts in the formed and stabilized core material emulsion; that means that urea, ammonium, and resorcinol are firstly dissolved in the solution with desirable surfactant, and then the core material is added and stabilized under vigorous agitation. After emulsion stabilization, formaldehyde is subsequently added and the pH and temperature are adjusted for polymerization. In the case of two-stage process, pre-polymers are formed under base-catalyst and are added to the stabilized emulsion of core material. Thereafter, the medium is acidified and heated, and the polycondensation starts rapidly.

Apart from DCPD, many other core materials, for example, epoxy[63,64] and 1H,1H′,2H,2H′-perfluorooctyl triethoxysilane (POTS),[65] have been explored using PUF microcontainers. However, in the above cases, catalysts are needed and the required proper ratio of catalysts to monomers has to be met, greatly limiting the options available. In this sense, catalyst-free polymerizable materials are highly desirable for a guaranteed self-healing behavior. Drying oils, which are water-insoluble unsaturated glycerides of long chain fatty acids, can be oxidized by contact of air to form a polymer film to heal the crack for corrosion protection, and have attracted great research interest. Linseed oil[66,67] and tung oil[68] have well demonstrated the success of this idea. Water-reactive organic healing agents have also emerged as promising candidates as catalyst-free polyemerizable agents. Silyl ester, is an reported innovative core material that can be triggered by water.[69] The core material is capable of reacting with water/humidity and metallic substrate, and thus no catalyst or crosslinker is needed.

Isocyanates provide another possibility for catalyst-free healing agents for their water reactivity.[70] Isophorone diisocyanate (IPDI) was studied for this purpose.[71] To obtain a better dispersion of the microcapsules containing IPDI in the alkyd varnish coating (AVC), Wang et al. further modified the PUF microcontainers with oxygen plasma to produce hydroxyl, carboxyl, and carbonyl groups.[72] The IPDI-AVC system was coated on 5083 aluminum alloy, titanium, copper, and Q235 steel surfaces for self-healing performance evaluation in seawater. The scanning micro-reference electrode (SMRE) technique able to provide an in situ imaging of the corrosion potential with time and spatial resolutions was employed to monitor the self-healing process of IPDI-AVC (20 μm thick) on Q235 steel substrate. Potential distribution of the steel surface was made possible by measuring the potential differences between a scanning micro-probe and a micro-reference electrode after the exposure of metal surface to seawater by a man-made scratch. Compared to pure AVC-coated metal, smaller potential differences were observed for the IPDI-AVC coated sample in the initial 4 h and no more potential signal was obtained after 12 h, suggesting a gradual self-healing process arising from isolative polymer films formed by IPDI monomers, Fig. 2. The self-healing time of IPDI-AVC was found dependent on the metal substrates. For example, active metals such as Q235 steel are not beneficial for self-healing process; interestingly, due to the formation of a thin metal-oxide layer on the metal surface, other metals including 5083 aluminum alloy, titanium, and copper, have much less influence on the self-healing time of IPDI-AVC system.

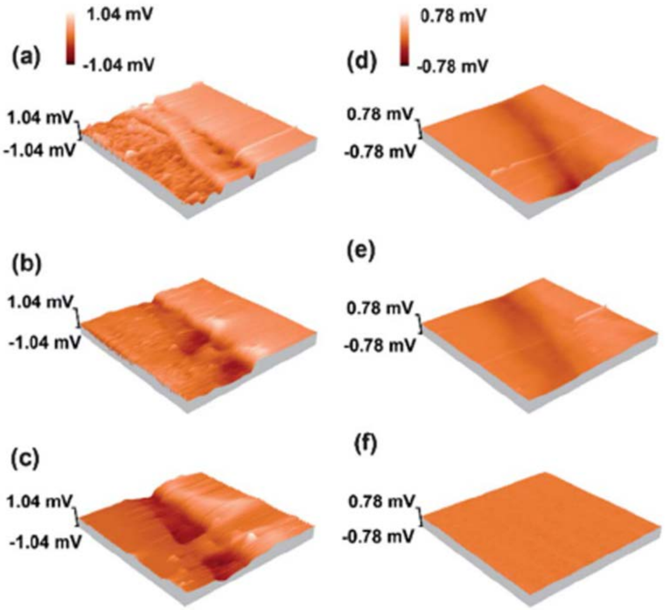

Fig. 2 Potential mapping above scratched Q235 steel substrates covered with AVC (a–c) and IPDI-AVC (d–f) measured by SMRE (2×2 mm). (a and d) correspond to an immersion time of 0.5 h, (b and e) to 4 h, and (c and f) to 12 h in 0.01 M NaCl solution. The potential was measured 10 mm above the sample surface. Reproduced from (Ref. 72) with permission of The Royal Society of Chemistry.

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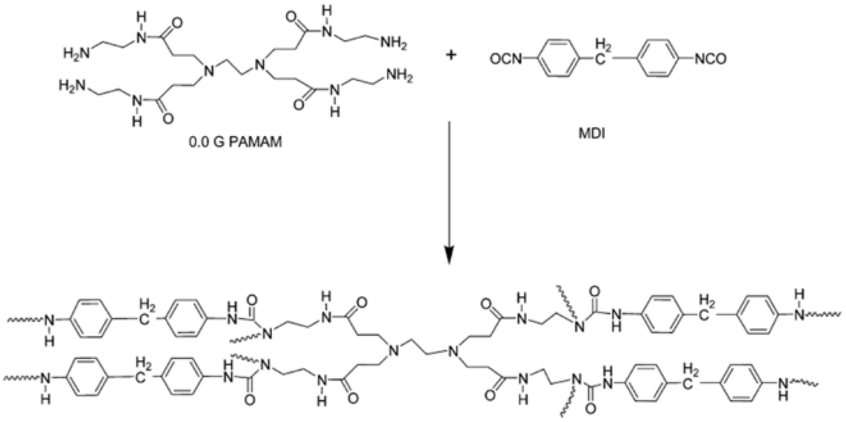

Fig. 3 Proposed mechanism for the reaction between PAMAM and MDI to yield polyurea microcapsule shell. Reprinted with permission from (Novel Polyurea Microcapsules Using Dendritic Functional Monomer: Synthesis, Characterization, and Its Use in Self-healing and Anticorrosive Polyurethane Coatings). Copyright (2013) American Chemical Society.

Recently, novel polyurea microcapasules from polyamidoamine (PAMAM) dendrimer of zero generation (0.0 G PAMAM) with commercial aromatic diisocyanate (MDI) were prepared, Fig. 3.[73] 0.0 G PAMAM was synthesized beforehand by amidation of tetra ester that was obtained by Michael addition reaction between ethylenediamine (EDA) and methacrylate. An interfacial polymerization of O/W emulsion technique was employed for preparation of the microcapsules. Briefly, aqueous solution containing polyvinyl alcohol (PVA, protective colloid) was mixed with xylene organic phase containing linseed oil (core material) and MDI to form a stable emulsion under different repititions per min (3000, 5000, and 8000 rpm). Then PAMAM in PVA aqueous solution was added to the above emulsion dropwisely for polymerization. The results suggest 55 wt% loading of the core material and the mean particle size of the resulting microcapsules was 266, 147, and 24 μm at 3000, 5000, and 8000 rpm, respectively. The chemical bonds between the isocyanates in the PU matrix and the amine groups in the microcontainer provide good strength and better interfacial interaction between the capsules and the matrix. The best performance was found with 5 wt% loading of microcapsules in the accelerated corrosion immersion test in 5% NaCl aqueous solution.

Polyurethane (PU) is another commonly used polymeric shell for micro/nanocapsules. Similarly, PU containers are produced by interfacial polymerization where species containing multiple isocyanate groups dissolved in one phase of the emulsion interacting with polyalcohols dissolved in the second immiscible phase. The encapsulation of active material happens “in situ” simultaneously with the formation of the polymeric shell of the containers. PU microcapsules loaded with water-born PU[74] and hexamethylene diisocyanate (HDI) for catalyst-free self-healing[75,76] have been studied. Until now, all the anticorrosion mechanisms are mainly based on the passivation of the metal surface or creating a new isolative physical barrier by the corrosion inhibitors or sealants in the crack local area. Differed from the above mechanisms, a new concept is proposed by the synergistic combination of the passivation effect of the resulting film with its water-repelling properties to protect the metal.[77] As illustrated in Fig. 4, organofunctional silanes (alkoxysilanes) possessing a long hydrophobic tail will be encapsulated in the PU microcontainers. Once the coating is damaged, the released alkoxysilanes will form covalent bonds with the hydroxyl groups on the metal surface when exposed to an ambient medium with high humidity and form inactive electrochemical films to protect the metals. Meanwhile, the highly hydrophobic properties derived from the long hydrocarbon tails prevent the penetration of water and aggressive ions. Both nano/microcapsules can be prepared by varying the stirring speed in the emulsification step. The self-healing performance was evaluated via SVET measurements by embedding the micro/nanocapsules in water-born epoxy coating matrix (~20 μm) on aluminium alloy plate. The results suggest effective anticorrosion properties of the coatings even after three days immersed in 0.1 M NaCl.

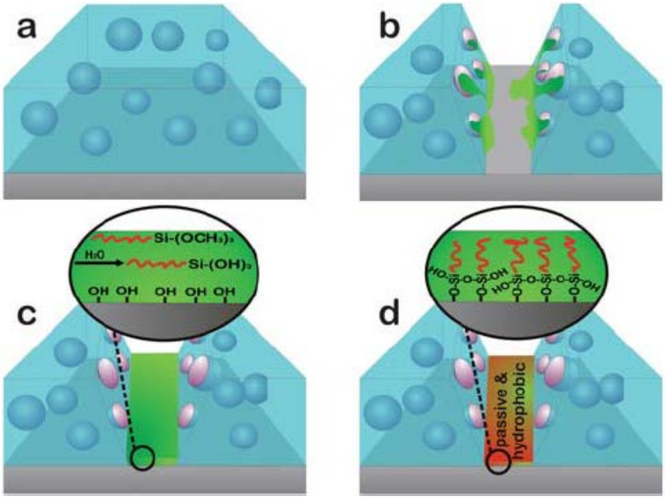

Fig. 4 Scheme of the self-healing process. (a) Self-healing coating containing microcontainers carrying alkoxysilanes mixture on a metallic substrate. (b) Damage of the coating; release of

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encapsulated material on the metal surface. (c) Reaction of alkoxysilanes with water from the ambient environment. (d) The damaged surface becomes passive and hydrophobic due to the binding of silanes with a long hydrophobic tail. Reproduced from (Ref. 77) with permission of The Royal Society of Chemistry.

Meanwhile, PU/PUF bilayers have also been studied for microcontainers.[78] The double layer brings substantial improvements to the microcapsule properties compared to single PU or PUF wall. The inner PU layer provides the flexibility while the outer PUF provides the desired strength, which enables higher effective loading of the microcapsules in the coating matrix.

Other innovative polymeric containers involve polystyrene (PS). Li et al.[79] studied the pH-responsive PS nanocontainers loaded with corrosion inhibitor benzotriazole (BTA) for self-healing anticorrosion coatings. BTA is encapsulated in the PS during the polymerization process, which is followed by adsorption of highly branched polyethylenimine (PEI) layer for a regulated release of inhibitors in response to external pH stimuli as well as for avoiding BTA leakage, Fig. 5A. The nanocontainers exhibit well defined morphology and a narrow size distribution with a polydispersity index ranging from 1.004 to 1.019, Fig. 5B&C. The nanocontainers have an excellent compatibility with epoxy organic coating matrix. The release of the inhibitors is triggered by the pH changes caused by the electrochemical corrosion reactions, and the SVET measurements demonstrate a fast self-healing process and remarkable corrosion resistance for the nanocapsules doped epoxy coating. The facile synthesis, cost-effective, and easy upscale for industrial applications of this approach promises broad future perspectives; however, the drawback with the PS nanocontainers is their poor compatibility with sol-gel inorganic coatings, which limits their applications for only organic coatings.

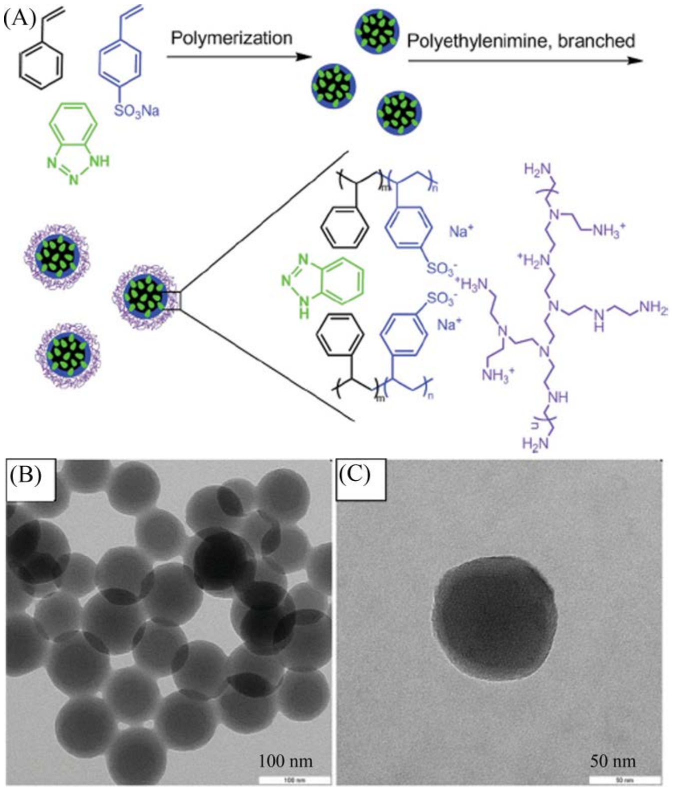

Fig. 5 (A) Illustration of the synthesis of corrosion inhibitor-loaded PS-BTA/PEI core–shell polymeric nanocontainers; TEM images of the PS-BTA/PEI core–shell nanocontainers at (B) lower and (C) higher magnification. Reproduced from (Ref .79) with permission of John Wiley and Sons.

2.2 Inorganic clay based nanocapsules

Apart from organic polymeric micro/nanocontainers, inorganic clays have also attracted significant interest. The clays work via different mechanisms depending on their structures. Some with hallow or microparticle structure works similar to polymeric nanocontainers for encapsulating active materials. For example, halloysite (an aluminosilicate hallow tube with the empirical formula of $Al_2Si_2O_5(OH)_4$) and hydroxyapatite (a naturally occurring mineral form of calcium apatite with the formula $Ca_5(PO_4)_3(OH)$) microparticles are able to load corrosion inhibitors with its hallow tube or microparticle structures, Fig. 6.[53,80,81] To address the problem of lower loading efficiency (5-10 wt% for halloysite versus 40-60 wt% for polymeric capsules), lumen enlargement through selective alumina etching allowed for matching its loading efficiency to polymeric capsules.[82]

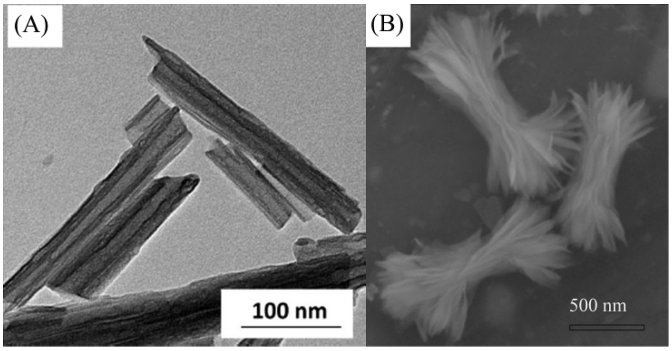

Fig. 6 (A) TEM image of halloysite nanotubes. Reprinted with permission from (Self-Healing Coatings Based on Halloysite Clay Polymer Composites for Protection of Copper Alloys). Copyright (2013) American Chemical Society. (B) SEM images of hydroxyapatite microparticles. Reprinted with permission from (Hydroxyapatite Microparticles as Feedback-Active Reservoirs of Corrosion Inhibitors). Copyright (2010) American Chemical Society.

Ion-exchange clays are another type of clays of significant importance for their ability to release inhibitive ions or sequester aggressive ions such as chloride when encountered a corrosive environment. Releasing the active materials is provoked by the presence of corrosive chloride ions and proceeds via ion-exchange reactions. Cation-exchange systems from clays including zeolites and naturally occurring bentonite clay minerals have been more widely studied. For example, Williams et al. investigated the smart release of group II and Zn(II)-exchanged bentonite capsules for the inhibition of corrosion-driven organic coating disbondment on galvanized steel.[83] Electrolyte penetrates through the defects in the organic coatings on iron and zinc substrates and form an underneath thin layer where a “delamination cell” is established, Fig. 7A. The delamination cell couples the anodic metal dissolution to cathodic oxygen reduction. The alkaline environment at the cathode drives coating disbondment through dissolution of amphoteric oxide layers, polymer degradation, and hydrolysis of interfacial bonds. Studies show that the bentonite capsules containing trivalent rare earth and alkaline earth cations (Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}) are able to specifically inhibit corrosion-driven cathodic disbondment by stifling cathodic oxygen reduction. The inhibition of corrosion-driven coating disbondment derives from the exchange of Na^+ in the underfilm electrolyte layer with the group II cations from the bentonite, Fig. 7B. The possible subsequent hydrolysis or partial hydrolysis of the exchanged group II aquo-cation in the alkaline environment may cause reduced electrical conductivity and ion mobility, therefore leading to decreased cathodic disbondment rates, as demonstrated, Fig. 7C. The development of scanning Kelvin probe technique (SKP) allows a spatial and temporal resolution of potential distributions beneath the organic coatings and greatly facilitates studying the efficiency of the ion-exchange bentonite in slowing the delamination kinetics and helping the healing process.

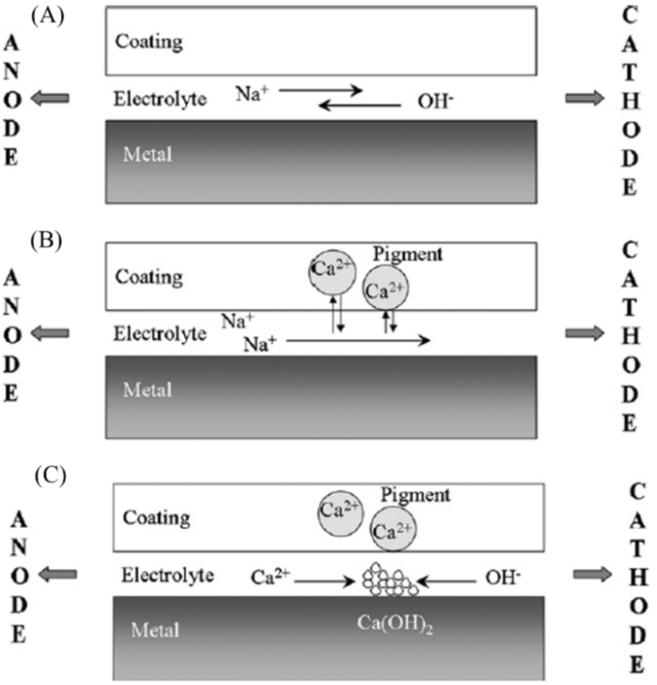

Fig. 7 Schematic representation of inhibition of corrosion-driven delamination on the iron or zinc substrates. (A) Ion transport in the presence of Ca^{2+}-exchanged bentonite pigment, (B) cation exchange and (C) cation hydrolysis at elevated pH in the absence of Ca^{2+}-exchanged bentonite pigment. Reproduced from (Ref. 83) with permission of Elsevier Ltd.

Layered double hydroxide (LDH) nanocontainer, also known as anionic clays or hydrotalcite (HT)-like compounds, are typical anion-exchange materials that consist of stacks of positively charged mixed metal hydroxides layers, between which anionic species and solvent molecules are intercalated. LDH is expressed by the general formula of $[M_{1-x}^{z+}, M_x^{y+}(OH)_2]^{a+}(A_{a/n}^{n-}) \cdot mH_2O$, where the cations M^{z+} (z = 1 or 2) and M^{y+} (y = 3 or 4) stay in the octahedral holes in a brucite-like layer, and the anion A^{n-} is located in the hydrated interlayer galleries.[84] The ability of delivering anions makes it possible to intercalate organic anion inhibitors, for example, vanadate ($V_2O_7^{2-}$)[85] and molybdate (MoO_4^{2-})[86] between hydroxide layers of LDH. The anion-exchange micro/nanocapsules can play a double role in absorbing the harmful chlorides and releasing the inhibiting ions in response to corrosion onset.[87] For example, Zheludkevich et al.[88] prepared two Zn/Al and Mg/Al hydroxides loaded with vanadate anions, denoting as ZnXAlY or MgXAlY, where X stands for the nominal Zn/Al or Mg/Al atomic ratio and Y for the interlayer anion of vanadate. Two methods have been employed to prepare the capsules, i.e., direct synthesis in the presence of corrosion inhibitor and the anion exchange of NO_3^- containing LDH precursor with vanadate containing solution. The capsules were added into commercial non-inhibited water-based epoxy primer and then topcoated with a water-based epoxy on aluminum alloy 2024 for performance test. Both immersion corrosion test in 0.05 M NaCl aqueous solution (50 mg per 10 mL) and standard accelerated corrosion tests including filiform corrosion test (FFT) performed according to EN ISO 3665, salt spray test (SST) performed according to ISO 9227, and Q-Panel condensation test (QCT) according to ASTM D 4585–99 were performed. The results show that the Zn/Al LDH prepared by anion-exchange method confers the best active corrosion protection and the addition of Zn/Al LDH nanocapsules into commercial primer on aluminum alloy substrate for aeronautical applications leads to a significant improvement. However, the problem with LDH based nanocapsules is their less effective corrosion protection compared to the chromate-based pigment and its practical usefulness remains unproven.

Till now, most self-healing coatings are mainly designed for protection of single material. However, the wider utilization of hybrid structures consisting of joined dissimilar materials, for example, aluminium alloy AA6061 for new generation of cars and aircrafts, calls for the advances in self-healing protection. For example, high risk galvanic corrosion exists in the hybrid materials due to their very different electrochemical potentials in the hybrids. Maria et al.[89] reported the corrosion protection of aluminum alloys and carbon fiber reinforced plastic (CFRP) by combination of anion-exchange LDH loaded with BTA- and cation-exchange bentonite loaded with Ce^{3+} in the same coating system. The inhibitors loaded with nanocontainers were embedded in commercial available bi-component epoxy resin (SEEVENAX, Mankiewicz) with approximately 2 wt% with respect to the dry film. The SVET results proved the self-healing properties from the BTA- and Ce^{3+} released from LDH and bentonite, respectively, Fig. 8. The protection mechanism is that the cathodic sites were blocked by the insoluble hydroxide layer under local alkalinized environment from Ce^{3+} cations that were released by cation-exchange with Na^+ and Al^{3+} (coming from anodic dissolution) while the LDH releases inhibitors and traps the corrosive agent Cl^- once the corrosion begins.

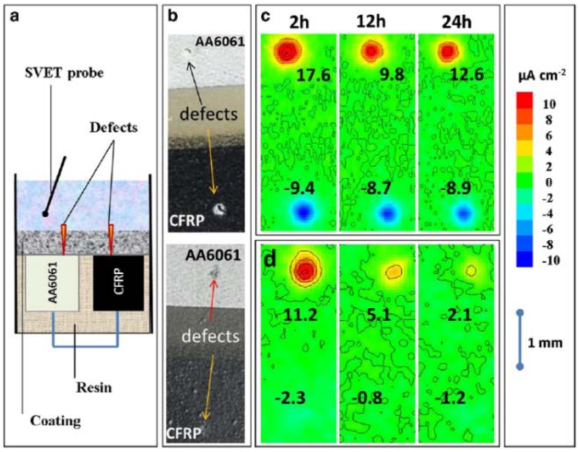

Fig. 8 (a) Scheme of AA6061+CFRP microelectrode concept, (b) microphotographs of coated galvanic cell with artificial defects. SVET maps for (c) the sample with blank coating and (d) the coating

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loaded with combination of nanocontainers (LDH-BTA + bentonite-Ce^{3+}) obtained after 2, 12 and 24 h of immersion in 0.05 M NaCl. Reproduced from (Ref. 89) with permission of Elsevier Ltd.

2.3 Mesoporous silica based nanocapsules

Hollow mesoporous silica nanoparticles (HMSNs) have attracted much attention as potential nanocontainers due to their high stability, biocompatibility, large specific surface area, governable pore diameter, and easy surface functionalization. For example, Borisova et al. studied the concentration and position of the mesoporous silica nanocontainers loaded with 2-mercaptobenzothiazole (MBT@NCs) in a hybrid sol-gel (SiO_x/ZrO_x) layer coated on an industrially important aluminum alloy AA2024-T3.[90,91] The effect of the concentration of embedded NCs on the coating anticorrosion efficiency was determined to be a critical factor. Too low concentrations (0.04 wt %) led to good coating barrier properties but unsatisfactory active corrosion inhibition because of an insufficient amount of available inhibitor. On the contrary, too high concentrations (0.8−1.7 wt %) deteriorate the coating integrity by introducing diffusion paths for aggressive electrolyte species, resulting in a loss of anticorrosion efficiency. A best passive and active corrosion resistance was provided by the coating containing 0.7 wt% MBT@NCs, as determined with EIS and SVET analysis. As to the position of the nanocapsules to the metal substrate, it's found that introducing the MBT@NCs into primer that's close to the metal surface facilitates a fast transport of released inhibitor upon corrosion attack and improves the active corrosion resistance and self-healing ability. Yet, better barrier properties are observed with MBT@NCs located in the top layer because of a preserved coating integrity and good adhesion between coating and metal surface. By analyzing the synergetic effect of inhibitor amount and path length on the metal surface considering factors including optimum barrier properties, active protection and adhesion, this study improves the understanding of the factors influencing the overall performance of the active anticorrosive coatings and enables the development of a coating system with optimum anticorrosion efficiency.

The abundant silanol groups (Si-OH) on the pore surface provide the possibilities for a controlled release system by various organic silanes modification. One method to convert mesoporous silica nanoparticles into mechanized silica nanoparticles by the installation of supramolecular nanovalves has been proposed. The rotaxanes or pseudorotaxanes nanovalves on the mechanized silica nanoparticles transit from “close” to “open” state via the movement of macrocycles non-covalently linked to the axle molecules upon a specific stimulus of pH, electricity, light, enzyme, and redox activation.[92] Chen et al. modified the HMSNs with 3-chloromethyl triethoxysilane (CMTES)/1,4-butanediamine (BDA) and Nphenylaminomethyltriethoxysilane (PhAMTES) to obtain the alkaline and acid-responsive MSNs, respectively, Fig. 9.[93]

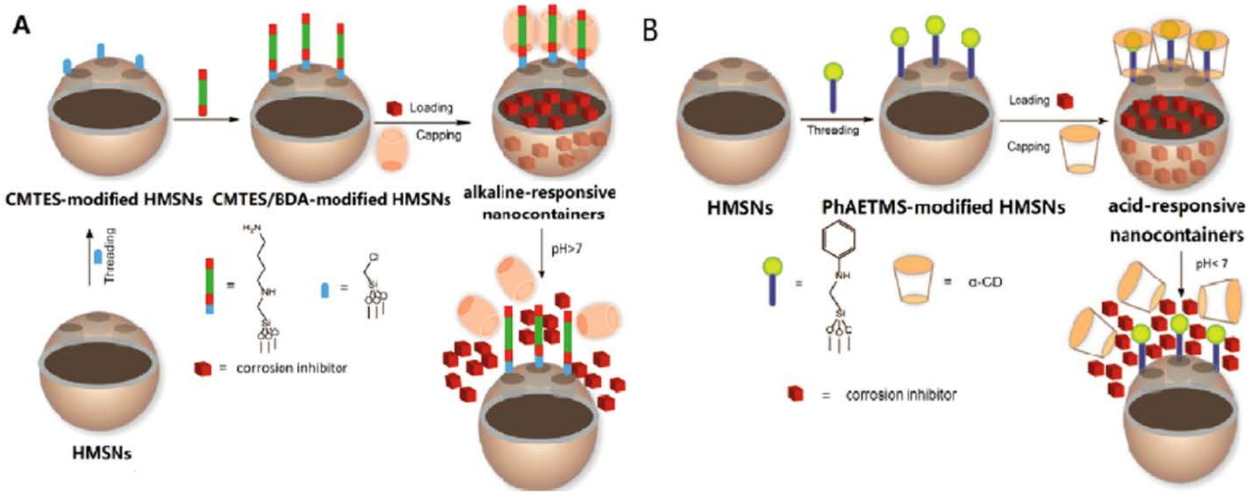

Fig. 9 Graphical representations of the synthesis and operation of (A) alkaline- and (B) acid-responsive nanocapsules. Reproduced from (Ref. 93) with permission of IOP Publishing Ltd.

With the development of the rotaxane molecular switch assembled by the water-soluble macrocycles such as cyclodextrin and cucurbit[n]uril (CB[n]), the use of supramolecular nanovalves extends from organic solvent to water solution. Acid and alkaline dual stimuli-responsive mechanized hollow mesoporous silica nanoparticles have been successfully designed using HMSNs as solid supports and the bistable CB[7]/hexylammonium unit-ferrocenecarboxylic acid unit pseudorotaxanes as supramolecular nanovalves, Fig. 10.[94] The self-assembled nanophase particles coating doped with nanocontainers with acid and alkaline dual stimuli-responsive characteristics demonstrated excellent self-healing functionality for aluminum alloy AA2024 by not only delayed the penetration rate of corrosive species but also repaired the damaged aluminum oxide layer to maintain the long-term anticorrosion behavior.

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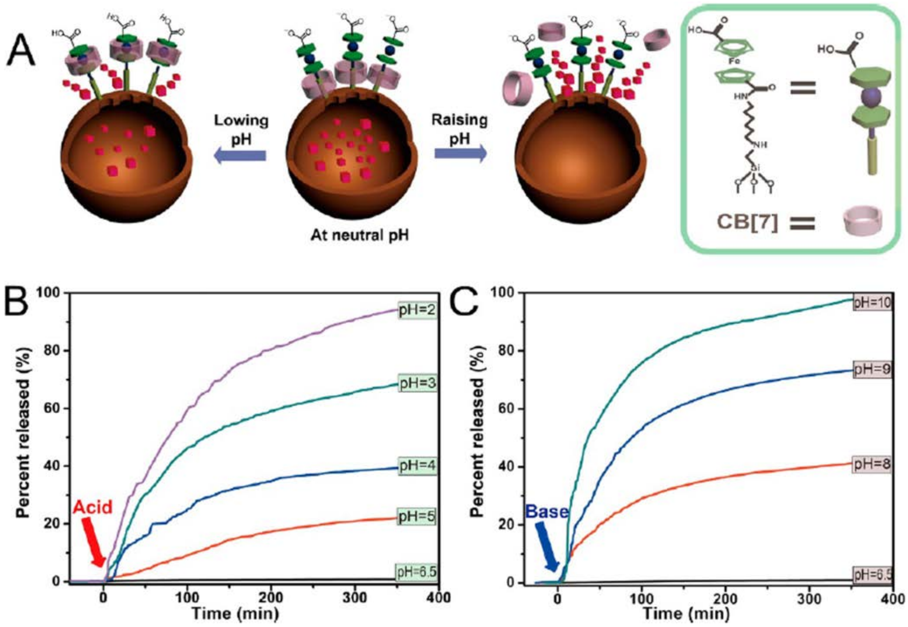

Fig. 10 (A) Schematic illustration of the working principles for the mechanized HMSs; release profiles of caffeine molecules from the mechanized HMSs under (B) acidic and (C) alkaline conditions. Reprinted with permission from (Acid and Alkaline Dual Stimuli-Responsive Mechanized Hollow Mesoporous Silica Nanoparticles as Smart Nanocontainers for Intelligent Anticorrosion Coatings). Copyright (2013) American Chemical Society.

2. 4 Polyelectrolyte multilayer based nanocapsules

Polyelectrolyte multilayers opens new opportunities for self-healing anticorrosion protection.[95] The sensitivity of the polyelecrolyte film to a variety of physical and chemical conditions like pH-shift or mechanical impact of the surrounding media provides the ability of a controlled release of the inhibitor species entrapped into multilayers. Polyelectrolytes are usually assembled on the surface of nanoparticle substrates via a layer-by-layer (LBL) approach. The LBL deposition procedure involves the stepwise electrostatic assembly of oppositely charged species on the substrate surface with nanometer scale precision and allows the formation of a coating with multiple functionalities. The coating properties can be controlled by the number of deposition cycles and the types of polyelectrolytes used. The conformation of polyelectrolytes is mostly dependent on their nature and adsorption conditions and much less dependent on the substrate and charge density of the substrate surface. The inhibitors will be released in a controllable way from the host structure when the conformation of the polyelectrolyte molecules changes induced by pH changes, Fig. 11.[96] Another release of the inhibitors can be achieved by the dissolution of reservoirs at desired pH at the anodic or cathodic sites. However, the method is confined to lab-scale and is far from industrialization due to the complex technologies involved.

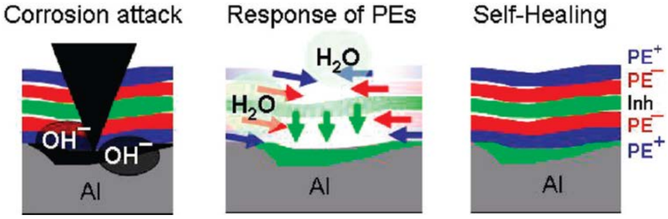

Fig. 11 Schematic mechanism of self-healing action of a “smart” polyelectrolyte anticorrosion coating. Corrosion attack causes pH changes of the system, which stimulates response of the polyelectrolyte coating: pH buffering, rearrangement of polymer chains, and release of corrosion inhibitor. PE^+, positively charged polyelectrolyte; PE^-, negatively charged polyelectrolyte; Inh, corrosion inhibitor. Reprinted with permission from (Layer-by-Layer Polyelectrolyte/Inhibitor Nanostructures for Metal Corrosion Protection). Copyright (2010) American Chemical Society.

2.5 Nanocapsules based on other nanocontainers

Innovative nanocapsules based on a new type of nanoctainer were reported by Chen et al. on the synthesis of mesoporous zirconia (*hm*-ZrO_2) with a hollow core/porous shell structure through a hard template method.[97] Initial work has been done by the release of inhibitors loaded in these monodispersed spherical particles (an average size of 400 nm) by pH stimuli, but further field testing is needed to evaluate the self-healing performances of these nanocontainers loaded with active materials in different coating matrixes.

Meanwhile, hybrid microcontainers have been investigated. Li et al. also reported silica/polymer double-walled hybrid nanocontainers consisting of a hollow cavity, a porous silica inner wall, and a stimuli-responsive polymeric outer wall for promising nanocontainers.[98] The silica/polymer hybrid nanotubes were prepared by surface-graft precipitation polymerization using double-bond modified nickel-hydrazine/silica core-shell rod templates followed by the etching of the nickel-hydrazine core. This approach makes it possible to fabricate nanocontainers with controllable release mechanism (pH, temperature, or redox reactions) by tuning the polymeric outer shells. For example, the nanocontainers can either be temperature responsive from a poly(N-isopropylacrylamide-co-methylenebisacrylamide) outer shell or redox responsive from a poly(poly(ethylene glycol) methacrylate-co-bis(2-methacryloyl)oxyethyl disulfide) outer shell, Fig. 12.

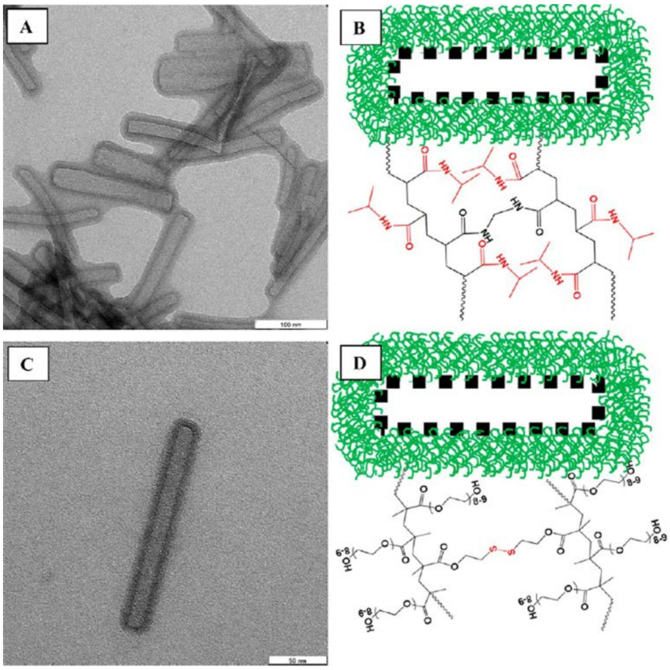

Fig. 12 TEM images and scheme of the temperature-responsive silica/PNIPAM (A and B) and redox-responsive silica/PPEGMA (C and D) hybrid nanotubes. The scale bar in A and C is 100 and 50 nm, respectively. Reprinted with permission from (Silica/Polymer Double-Walled Hybrid Nanotubes: Synthesis and Application as Stimuli-Responsive Nanocontainers in Self-Healing Coatings). Copyright (2013) American Chemical Society.

3. Conclusions and perspectives

This review gives the most recent development in various micro/nanocontainers loaded with various core active materials for smart self-healing coatings for metallic substrate protection. The design and preparation of polymeric and inorganic nanocontainers with versatile functionalities provide great opportunities for developing new generation of smart coatings with self-healing properties in response to different stimuli. Given the intrinsic presentence of pH gradient and water, pH- or wettability- responsive micro/nanocontainers are highly desirable. Meanwhile, green and innovative micro/nanocontainers from sustainable energy sources will gain more attention driven by increasing concerns over environment and limited reserves of fossil fuels. Furthermore, incorporating other functionalities such as self-cleaning, anti-dusting, and anti-fouling properties into the smart self-healing coatings will be promising for fabricating advanced coatings with combinatorial healing abilities and multifunctional properties.

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