Nanocontainer-Based Active Systems: From Self-Healing Coatings to Thermal Energy Storage

E. Shchukina, D. G. Shchukin*

Stephenson Institute for Renewable Energy, Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD, Liverpool, UK. E-mail: d.shchukin@liverpool.ac.uk.

ABSTRACT We highlight in our feature article the development of nanocontainer-based active materials started in 2006 in Max Planck Institute of Colloids and Interfaces under supervision of Prof. Helmuth Möhwald. The active materials encapsulated into the nanocontainers with controlled shell permeability have been first applied for self-healing coatings with controlled release of the corrosion inhibitor. The nanocontainers have been added to the paint formulation matrix at 5-10 % wt. concentration, which resulted in attaining coating autonomous self-healing ability. This research idea has attracted attention of many scientists across the world (>1500 publications during last 10 years) and has already been transferred to the commercialization level. The current trend in nanocontainer-based active systems is devoted to the multifunctionality of the capsules which can combine self-healing, antibacterial, thermal and other functionalities in one host matrix. This paper summarizes the previous research done in the

area of the nanocontainer-based active materials together with future perspectives of the capsule-based materials with antifouling or thermo-regulating activity.

INTRODUCTION

Development of the functional micro- and nanocontainers (or capsules) has attracted interest for various research areas such as biotechnology, medicine, cosmetics, catalysis and bulk multifunctional autonomic materials. The main advantage of the nanocontainers is the possibility to isolate the encapsulated active agent from the surrounding environment combined with the targeted release of it where and when it is needed. In general, research on nanocontainer formation and loading requires the ability to form a nanocontainer shell, which should be stable, permeable to release/upload materials, and should also possess other desired functionalities (magnetic, catalytic, conductive, targeting, etc.). One has to combine several properties in the shell structure and composition to achieve this goal. Depending on the nature of the "smart" materials (e.g., polymers, nanoparticles, nanocarbons) introduced into the container shell, various stimuli can induce reversible and irreversible shell modifications: variation of the pH, ionic strength, temperature ramp, ultrasonic treatment, alternating magnetic field, electromagnetic field. Different responses can be observed varying from fine effects like tunable permeability for molecular-sized corrosion inhibitors to the total rupture of the container shell.

Several approaches have been developed so far to fabricate micro- and nanocontainers.[1] One approach is based on self-assembly of lipid molecules or amphiphilic block copolymers into spherically closed bilayer structures (vesicles).[2,3] A second approach is to use dendrimers or hyperbranched polymers as nanocontainers.[4,5] The third procedure involves suspension and

emulsion polymerization around oil or water nanodroplets forming cross-linked polymer shell, also involving ultrasound. This method allows one to obtain hollow nanoshells with the size starting from 20 nm in a facile, one-step procedure. The method is well studied and several reviews exist on emulsion polymerization technique.[6,7] Contrary to the organic nanocontainers, inorganic nanocontainer scaffolds (like mesoporous silica or titania and halloysite nanotubes) with pH-controllable pore nanovalves are more mechanically robust and cheaper to be used in large scale production.[8,9] This feature review highlights the current achievements in the area of self-healing coatings, which has been started in 2006 in Max-Planck Institute of Colloids and Interfaces, Golm, Germany together with new trends in development of nanocontainer-based multifunctional materials. First part will contain the description of the autonomous self-healing coatings and their commercialization potential when the other parts will be focused on the added multifunctionalities like antifouling activity or heat storage property.

CONCEPT OF NANOCONTAINER-BASED SELF-HEALING COATINGS

The general approach to impart feedback functionality to a coating by the incorporation of encapsulated active material is represented in (Figure 1).[10,11,12] The possibility of interplay between shell properties, encapsulated active agent (inhibitor), coating formulation and metal substrate makes this approach almost universal for multifunctional coating solutions. However, the general concept faces difficulties in interaction between coating components and nanocontainer shell. There is no universal solution until now for nanocontainers loaded with corrosion inhibitors for the application in different types of the coatings Therefore, many types of nanocontainers are developed in scientific literature (we estimated around 200) but only a few

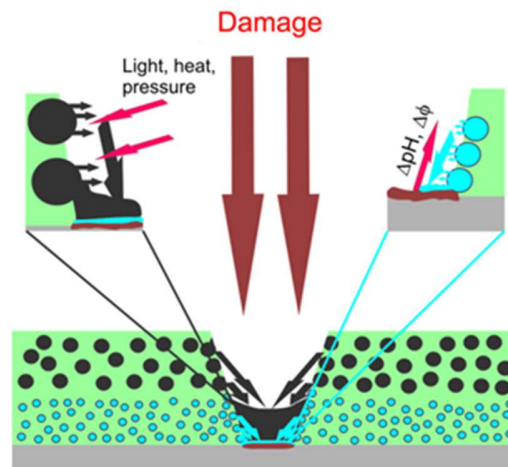are on the direct way for commercialisation. Here, we highlight the mostly developed self-healing systems.

Figure 1. Schematic representation of nanocontainer-based self-healing coatings.[10]

Nanocontainer-based self-healing coatings can be classified according to the external stimulus to which they respond. Various external stimuli of physical or chemical nature can cause a change in the coating followed by the self-recovery of the initial coating property:

1. Mechanical impact is a first external stimuli demonstrated for microcapsule-based coatings by White *et al.*[13] They encapsulated healing agent (dicyclopentadiene) in polymer microcapsules embedded in an epoxy coating matrix containing Grubbs catalyst. The embedded microcapsules are ruptured upon crack formation, and the healing agent is released into the crack by capillary forces and comes into contact with the catalyst. The result is in crack healing and recovery of the barrier properties of the coating. The next step in the mechanically-triggered self-healing coating

was the development of microvascular network[14,15] loaded with the reagents necessary to cure a healing polymer inside the crack. Another way is to use curing agent from the local environment employing highly air-sensitive or moisture reactive materials, such as metal oxide precursors[16] and organosiloxanes[17] as encapsulated cargo. In such coatings, the active material is first released due to the crack propagation and forms an impermeable layer only after oxidation and hydrolysis by atmospheric oxygen or water. Successful self-healing by such triggering mechanism requires capsule size large enough (50 - 200 µm) to enable easy rupture and delivery of sufficient amount of active agent. However, the integration of big microcapsules into thin coatings is limited by coating thickness. Microcapsule shells should be rigid to preserve the capsule integrity during embedding in the coating matrix, brittle enough to facilitate capsule rupture upon crack formation and, at the same time, the active agent should be of low viscosity and vapour pressure.

2. Electromagnetic irradiation belongs to the physical stimulus, which affects nanocontainer shell due to either local heating or photochemical reactions. Direct incorporation of photocatalytic TiO_2 particles into polymer coatings leads to the oxidation of the organic components of the coating matrix and loose of its barrier properties. However, application of TiO_2 and Ag nanoparticles as triggering component of the nanocontainer shell makes possible to release the encapsulated agent without the damage of the coating matrix. A polyelectrolyte shell, which modifies the outer surface of TiO_2-based containers, prevents the spontaneous leakage of the loaded material and revealed UV-stimulated release of benzotriazole corrosion inhibitor under UV-irradiation.[18] For the coatings where very fast release of the inhibitor is important, the use of UV-irradiation as an external trigger is strongly preferable. The similar effect, but with the slower inhibitor release, was found by Skorb *et al.* for nanocontainers coated with

polyelectrolyte shell containing IR-sensitive Ag nanoparticles.[19] One could terminate the corrosion process, in this case, by intensive local IR laser irradiation. The healing ability under laser irradiation was proven by the scanning vibration electrode technique (SVET). It was also noted that, by applying a polyelectrolyte shell with noble metal particles over the mesoporous titania via layer-by-layer assembly, it is possible to fabricate micro- and nanoscaled containers sensitive to both UV and IR irradiation.

3. Internal chemical impact from the coating/metal substrate interface to trigger the inhibitor release is the change of the local pH in the corroded area. It is currently most popular for nanocontainer-based self-healing coatings and the nanocontainers based on it were commercialised in Europe and China. Utilizing pH shift as stimulus for corrosion inhibitor release is the natural way to design anticorrosive coatings with high self-healing response because the corrosion leads to local pH decrease in anodic areas and local pH increase in cathodic ones. There are several ways to make pH-sensitive nanocontainers for self-healing coatings. The first developed one is layer-by-layer (LbL) assembly of oppositely charged species (*e.g.* polyelectrolytes) on templating colloidal nanoparticles. The template can be either removed to form a hollow structure or kept to provide better mechanical stability.[20,21] The advantages of this method are the variety of the charged species suitable for shell construction, the adjustable layer thickness and flexibility. For example, silica nanocontainers with benzotriazole (BTA) loaded LbL shell were dispersed in sol-gel coatings and demonstrated good corrosion resistance.[22] Another methodology to increase the amount of inhibitor in LbL nanocontainers is to incorporate the inhibitor in a porous core protected by LbL shell. This was demonstrated by inserting organic inhibitors into porous metal oxide nanoparticles (TiO_2 and SiO_2) and followed by their coating them with polyelectrolyte multilayers. Such pH sensitive nanocontainers were

dispersed in SiOx/ZrOx sol-gel coatings and improved the coating`s corrosion inhibition properties reducing corrosion to zero.[23] However, the complexity of such nanocontainers restricts their up-scaling and industrial application.

Commercially available porous inorganic materials can be applied as inorganic nanocontainers for self-healing coatings. Only inhibitor loading and formation of the trigger-sensitive blockers (valves) are fabrication steps required to produce ready-to-use inhibitor-loaded nanocontainers. Inorganic nanocontainers can be mesoporous silica[24] or titania,[25] ion-exchange nanoclays[26] and halloysite nanotubes.[27] Mesoporous silica and titania are commercial products and, despite they are produced in thousand tons volume, they are still more expensive than halloysites. The industrially mined, viable and inexpensive halloysite nanotubes have high potential as inhibitor nanocontainers for commercial applications. Halloysites are two-layered aluminosilicates with hollow tubular structure. Their size varies within 1-15 µm of length and 10-150 nm of lumen inner diameter. Halloysite nanotubes were loaded with the inhibitor, 2-mercaptobenzothiazole and covered by a polyelectrolyte stopper layer to improve the control over the inhibitor release.[28,29] Anticorrosion performance tests using the industrial neutral salt-spray test (ISO 9227 standard, 5 wt% NaCl, 35 °C) were conducted to check halloysite efficiency in industrial coatings.[30,31]
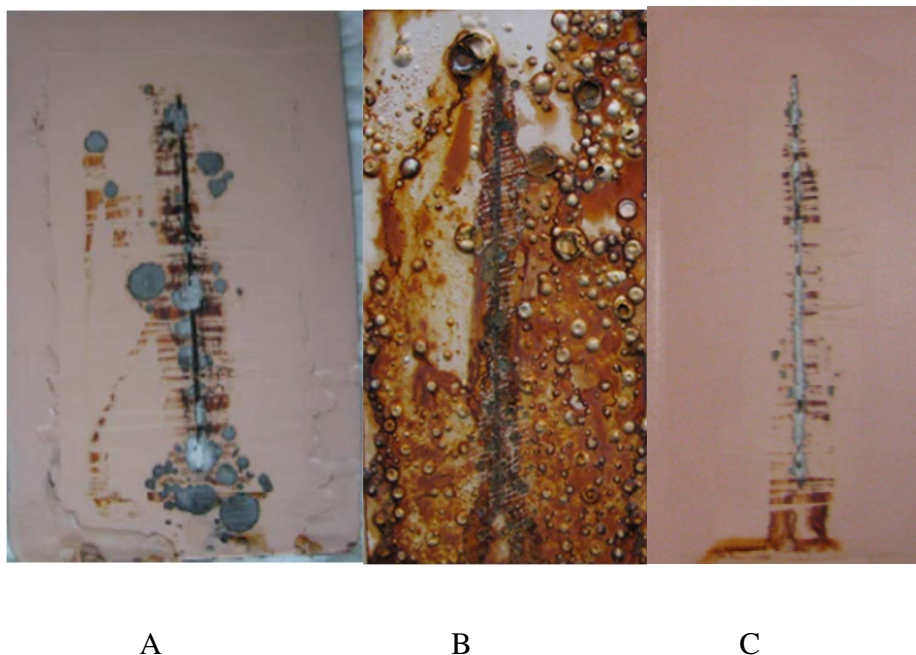
| A | B | C |

Figure 2. Neutral salt-spray test results for pure polyepoxy coating (A, 1000 h), polyepoxy coating directly loaded with Korantin SMK corrosion inhibitor (B, 500 h) and polyepoxy coating in the presence of Korantin SMK-loaded halloysite nanotubes (C, 1000 h).[31]

As one can see in Figure 2, direct addition of Korantin SMK corrosion inhibitor, which is an alkylphosphoric ester produced by BASF with a chain length of alkyls in the ester group ranging from C6 to C10, into the coating in free form (1 wt%) drastically reduces corrosion protection performance even after 500 h of the neutral salt-spray test. On the contrary, inhibitor encapsulated inside halloysite nanotubes increased corrosion protection by five times. These results are due to the favourable halloysite structure, which provides good inhibitor storage in the lumen and limits spontaneous inhibitor leakage due to the small-diameter (20-50 nm) ends covered by the pH-sensitive stoppers.[32] Salt-spray tests demonstrate clear evidence on an

industrial level that halloysite nanotubes can develop a new, revolutional generation of self-healing anticorrosion coatings on mass-production level.

4. More rare external triggers used for capsules and nanocontainers in self-healing coatings are: ultrasonic treatment;[33] temperature;[34] ionic strength;[35] and difference electrochemical potential on the surface of the corroded metal substrate under the coating matrix.[36,37,38,] However, only a few papers have been published in this field without continuous significant interest from academia and industry.

The current level of the nanocontainer development for autonomous self-healing coatings with single functionality or responsive only to one triggering mechanism already reached sufficient number of scientific publications on the laboratory scale and requires now the increase of the possible functionalities. However, the multiple functionality of the coatings may be limited by the amount of nanocontainers which can be incorporated into the coatings without changing their main properties like barrier, colour, etc. Usually, if the amount of nanocontainers exceeds 10 % wt. in the cured coating, its main passive properties become considerably reduced.[39] Therefore, the second generation of the multifunctional nanocontainer based coatings should involve nanocontainers with multiple functionality. This direction is rapidly developing now with increasing number of publications. In the next two parts, we would like to focus on two additional functionalities: (i) antofouling, which can be used for maritime applications and (ii) thermal energy storage for domestic applications, for example in zero-energy houses.

NANOCONTAINERS WITH ANTIFOULING ABILITY

Biofouling is a natural process that refers to the accumulation and growth of microorganisms, algae or plants on any natural or artificial wetted surface.[40] The first establishment by microorganisms and unicellular algae occurs within the first minute of immersion of the surface in seawater.[41] This initial stage allows the formation of a conditioning film consisted of physically adsorbed organic molecules followed by the settlement and growth of bacteria, protozoa and diatoms creating a complex biofilm matrix within the first 24 hours of immersion (microfouling). The existence of this complex biofilm provides sufficient food for the formation of microscopically visible algae, spores, seaweeds and invertebrates after 2-3 weeks of immersion (soft macrofouling). Finally, the increased capture of microscopically visible organisms stimulates the settlement of larvae of marine organisms such as mussels, barnacles, and sponges as well as spores of macroalgae after several weeks of immersion.[42] Biofouling in the maritime milieu leads to severe economic disturbances in the marine industries, as well as in a negative environmental impact. Biofouling is estimated to cost US$ 150 billion annually, a cost that is a result of the maintenance and cleaning of submerged man-made surfaces on buoys, membrane bioreactors, desalination units, cooling water systems and oil pipelines.[43] So, it is very important to stop biofouling on the first stage of the bacterial growth.

Historically, the most successful antifouling paints were biocide-based self-polishing coatings based on the well-known organotin compounds, especially tributyltin (TBT). However, its high toxicity on humans and the negative environmental impact led to the worldwide direct ban of the TBT usage by the International Maritime Organisation in 2008.[44] Therefore, the antifouling paint manufacturers were forced to study and develop TBT-free environmentally friendly antifouling paints. An effective methodology to address this problem is the controlled release of the encapsulated biocide, which controls the release rate of the biocides and, at the same time,

protect them from the surrounding environment.[45,46] If the surface of the nanocontainer is modified by the stable, not-releasing antifouling agent, the additional dual antifouling activity can be achieved – the first from the encapsulated biocide and the second one from the antifouling surface of nanocontainers.

The quaternary ammonium salts (QASs) were indexed as antimicrobial compounds for more than 70 years.[47,48] They were used against the growth of a broad range of microorganisms in several applications including food and pharmaceutical products, antiseptics, disinfectants, biocides, fungicides, cosmetics and water treatment.[49,50] The advantage of the QAS-modified materials is their attachable nature to the fillers of the coatings which allows a permanent antifouling effect of the coating without the release of the biocide material. Usually in the literature, non-porous silica nanocontainers are used only for the grafting of biocide agents on the surface and mesoporous silica nanoparticles (MSNs) only for biocide encapsulation. However, it is possible to demonstrate dual-function antibacterial/antifouling MSNs based on the combination of two strategies (surface modification and encapsulation) in one system (Figure 3).[51] For this purpose, spherical mesoporous MCM-48 silica nanoparticles with a dual synergetic antimicrobial effect were synthesised and tested against Gram positive and Gram negative bacteria as well as in antifouling coatings. For the preparation of MSNs, the modified Stöber's method was used according to Schumacher *et al.* because it is an easy and fast way to obtain MCM-48 at room temperature.[52] MCM-48 spherical nanoparticles were chosen for two main reasons. Firstly, their interwoven, branched 3D mesostructure makes them excellent candidates for the loading and release of biocides. Secondly, this is the first study that reports the surface modification of MCM-48 with QAS for secondary biocide activity and controlled release of encapsulated antifouling agent.
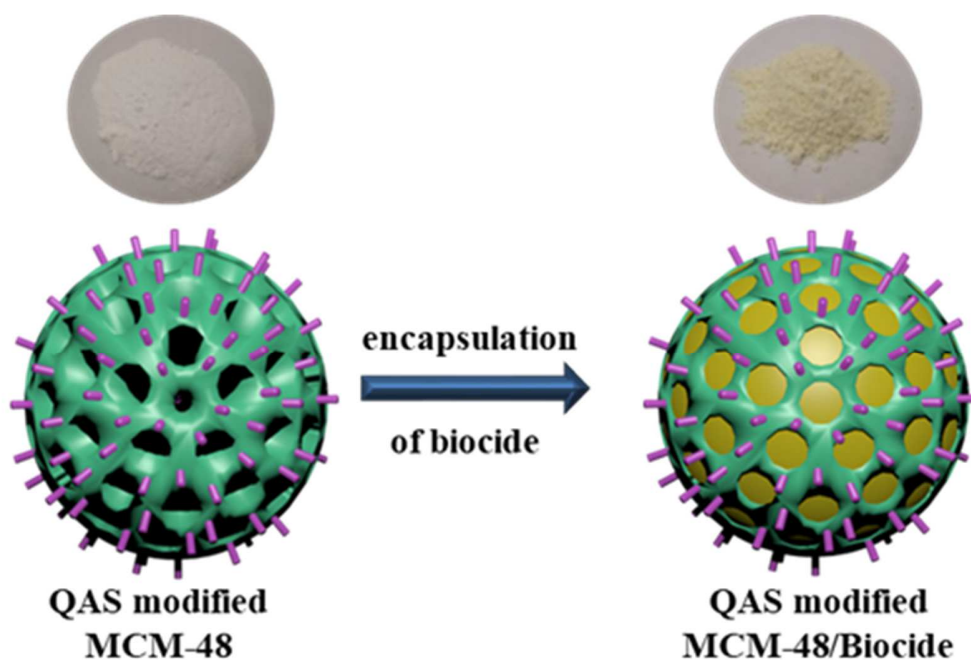
Figure 3. Encapsulation of biocide in the QAS-modified MCM-48 and solid materials before and after the encapsulation.

The specific surface area of the mesoporous MCM-48 nanocontainers exhibited high value of 1300 m^2/g. The average pore diameter was 3.2 nm. Encapsulation of eco-friendly Parmetol S15 biocide (active component DCOIT) reached 30% wt. yield. 22 mm x 22 mm glass slides were coated with a spin coater by using 1 mL of antifouling nanocontainers dispersed in ethanol solution (2% wt) and tested against *E. Coli* bacteria. As can been seen in the Figure 4, the QAS-modified MSNs reduced the number of the viable *E. Coli* by around 90 % as compared with the pristine MCM-48. Addition of the second functionality via Parmetol S15 encapsulation resulted in enhanced antibacterial performance by killing all the exposed bacteria during the whole test duration (at 37 °C for 3 hours).
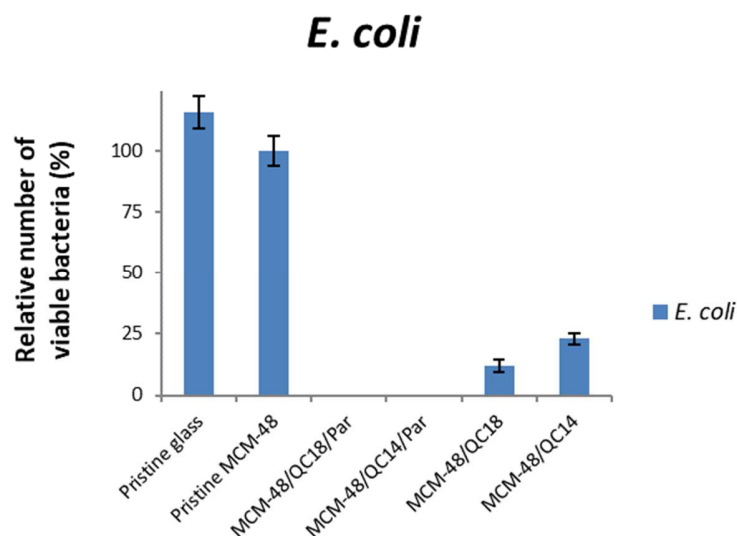
Figure 4. Relative number of viable bacteria (*E. coli*) after testing on glass slides spin-coated with pristine MCM-48, Parmetol S15 (Par) loaded/unloaded dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (QC18) and dimethyltetradecyl [3-(triethoxysilyl) propyl] ammonium chloride (QC14) surface-modified MCM-48.[51]

A panel field test took place in northern Red Sea, Eilat, Israel for five months period in order to evaluate the antifouling efficacy of the modified MCM-48 nanoparticles incorporated in ship coatings. PVC panels coated with pristine paint (biocide-free paint from Jotun, Norway) were used as control samples. Nanocontainers were suspended mechanically via a homogeniser in a polymeric paint matrix. The concentration of the nanoparticles in the paints was adjusted to 5% wt. and four different paint formulations were synthesised. Paint 1: pristine paint + 5% wt. QC18-modified MCM-48 and loaded with Parmetol S15; paint 2: pristine paint + 5% wt. QC14-modified MCM-48 and loaded with Parmetol S15; paint 3: pristine paint + 5% wt. QC18-modified MCM-48 and paint 4: pristine paint + 5% wt. QC14-modified MCM-48. The coated

PVC panels were placed on a floating structure made of a stainless steel frame submerged at a depth of 8-9 m. Figure 5 illustrates photographs of the exposed coated panels in the first day of deployment and after five months of exposure.
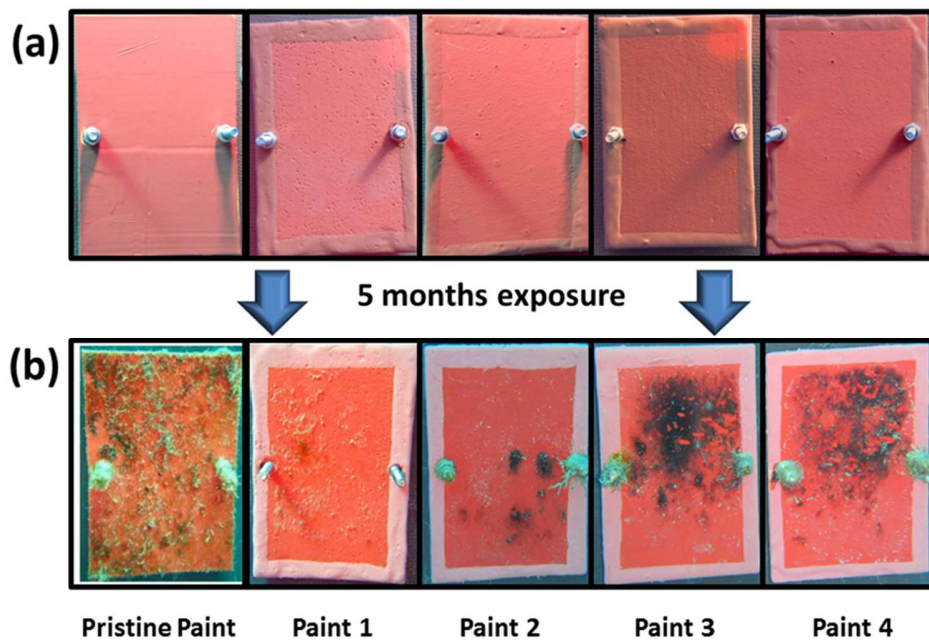

Figure 5. Photographs of PVC panels coated with pristine paint and paints 1-4 during the field test trial in Red Sea at the first day of deployment (a) and after 5 months of exposure (b).[51]

At the end of the field test, the control sample had 39% biofouling coverage while the paints 1-4 presented significantly lower biofouling coverage below 10%. Paints 1 and 2 containing the modified nanoparticles with the dual antifouling effect illustrated superior performance with 6.7% and 7.8% biofouling coverage due to the encapsulated biocide into the QAS modified

nanoparticles. The demonstrated results show a simple and facile approach towards multifunctional coatings combining self-healing and antifouling abilities.

NANOCONTAINERS FOR THERMAL ENERGY STORAGE

There are three main types of materials for thermal energy storage: materials for sensible heat storage (like water), materials for thermochemical heat storage where heat is converted into chemical energy and phase change materials where heat is stored as phase transition enthalpy. Solid-liquid PCMs show a good balance between energy capacity and volume changes upon phase transition. The ideal properties for a PCM are (i) suitable melting temperature, (ii) high latent heat, (iii) high thermal conductivity, (iv) congruent melting and no supercooling, (v) non-flammable, (vi) non-corrosive and (vii) low costs.[53] However, there are no PCMs found so far which fit all these criteria.

Mostly developed PCMs are organic paraffins and crystallohydrates.[54] Paraffin waxes are linear alkanes containing 8-40 carbon atoms. Their disadvantages include low thermal conductivity, flammability and high costs. Commercial paraffin contains formaldehyde and vinyl chloride as well as benzene, toluene, naphthalene and methyl ethyl ketone which are volatile and carcinogenic in nature, so care must be taken while using this materials in building applications.[55] Salt hydrates (also known as crystallohydrates) are the major class of inorganic PCMs, and most promising for applications due to their high latent heat, high energy storage density, low costs, and wide range of melting temperatures available. Disadvantages of salt hydrates include incongruent melting, phase separation, supercooling and corrosiveness towards container materials (heat carriers), especially metals. Incongruent melting is incomplete melting

of the salt hydrate, leading to the irreversible formation of a salt of lower hydration number. This leads to zero latent heat and also rendering salt hydrates chemically unstable often after very few melting/freezing cycles.

The practical use of PCMs is hindered by their limitations. The encapsulation of PCMs into the micro and nanocontainers can considerably improve energy storage properties (Figure 6). However, nanocontainer shell must possess "smart" multifunctional properties: controlled thermal energy release, protection against corrosion and degradation during heat uptake/release cycles, increased environment/PCM surface area and heat conductivity and, the last but not the least, possibility to use such energy capsules in powder or paste form as additives to the bulk materials (concrete, foam, paint, etc.) to attain them thermal energy storage properties.[56] All these properties are crucial to PCM usage in practical applications, so encapsulation can almost be as a 'one size fits all' solution.
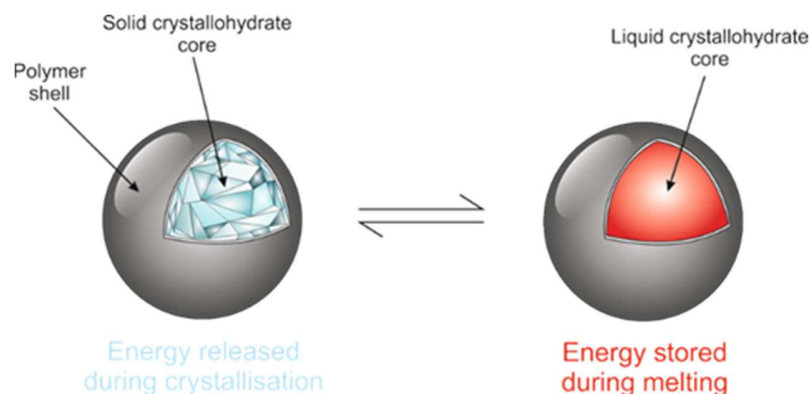

Figure 6. Cartoon showing ideal capsule behaviour for the salt hydrate core.[54]

Inverse Pickering emulsion, interfacial polymerisation and solvent evaporation–precipitation methods are the most common chemical ones described in the literature for the encapsulation of

the inorganic PCMs.[57] The first successful core-shell capsules containing salt hydrates specifically for energy storage were developed by Sarier *et al.* for thermally regulating fibres.[58] They have used a mix of PEG1000, hexadecane and sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) as core material encapsulated in a urea-formaldehyde shell. Salaün *et al.* encapsulated $Na_2PO_4 \cdot 12H_2O$ in a polyurea/polyurethane shell.[59] They used the solvent evaporation technique, dissolving cellulose acetate butyrate in a volatile solvent (chloroform) which polymerises as the solvent evaporates. The crystallohydrate load was up to 79% wt. Graham *et al.* demonstrated a simple method to nanoencapsulate magnesium nitrate hexahydrate, employing an *in situ* miniemulsion polymerisation with ethyl-2-cyanoacrylate as monomer.[60] Using sonication to prepare miniemulsions improved the synthesis by reducing the amount of surfactant required as stabiliser and then inverse miniemulsion polymerisation method was performed for encapsulation of magnesium nitrate hexahydrate nanodroplets resulting in 100-200 nm PCM nanocapsules. Figure 7 visually demonstrates stabilised PCM after encapsulation.
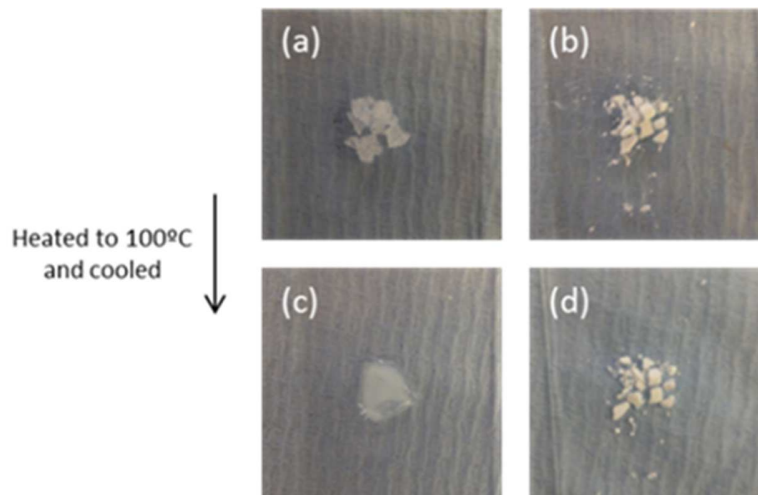

Figure 7. Bulk $Mg(NO_3)_2 \cdot 6H_2O$ (a & c) and nanoencapsulated salt hydrate (b & d) before heating to 100 °C (top), and after cooling back to room temperature (bottom).

Before melting, pure $Mg(NO_3)_2 \cdot 6H_2O$ is a crystalline solid (Figure 7a). After melting, it recrystallizes to the solid surrounded by water, showing a volume change occurs during phase transition and the recrystallized solid forms a compact block (Figure 7c). Nanoencapsulated salt hydrate (Figures 7b and d) shows no volume increase or change in appearance before and after heating to 100 °C. This indicates chemical and structural stability of the encapsulated PCM at the transition temperature. The absence of leakage means the salt hydrate is fully protected by encapsulation, which is consistent with the thermal stability demonstrated by DSC.

Formation of the crystallohydrate eutectics provides an effective instrument to regulate the melting temperature for desired applications.[61] The following paper describes the encapsulation of crystallohydrate eutectic mixture ($Mg(NO_3)_2 \cdot 6H_2O$ and $Na_2SO_4 \cdot 10H_2O$).[62] SEM images of the nanocapsules are shown in Figure 8. Initial crystallohydrates are large >1µm crystals combined into agglomerates up to 100 µm in size.
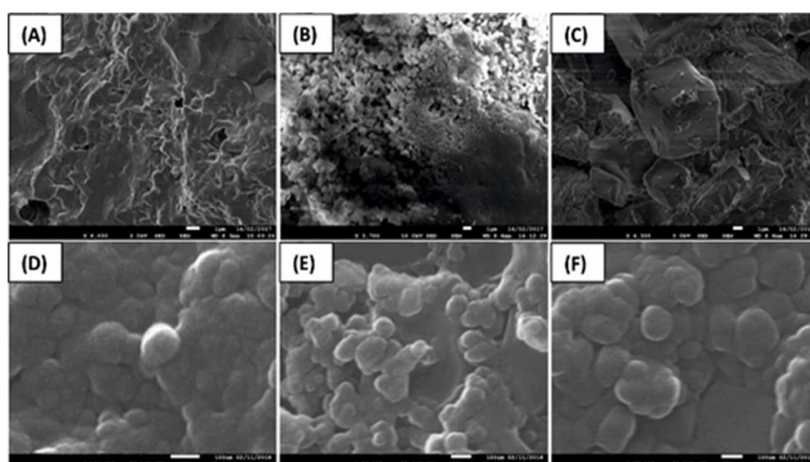

Figure 8. SEM images of bulk $Mg(NO_3)_2 \cdot 6H_2O$ (A), $Na_2SO_4 \cdot 10H_2O$ (B) and 1:1 % wt. $Mg(NO_3)_2 \cdot 6H_2O : Na_2SO_4 \cdot 10H_2O$ mixture (C). (D), (E), (F) demonstrate energy nanocapsules

with Mg(NO$_3$)$_2$·6H$_2$O, Na$_2$SO$_4$·10H$_2$O and 1:1 %wt. Mg(NO$_3$)$_2$·6H$_2$O:Na$_2$SO$_4$·10H$_2$O core, respectively. Scale bar for (A)-(C) images is 1 µm; for (D)-(F) images is 100 nm.[62]

After encapsulation, the size of the crystallohydrate core is reduced to 100-200 nm with the smooth capsule shell providing complete coverage of the core, with no pores present. This is important for ensuring the core material is protected from the environment and prevention of water loss during heating. The images show how the nanocontainers tend to aggregate, however single nanocontainers can be clearly seen. The non-spherical shape of the nanocontainers is caused by solid form of the crystallohydrate core appearing after cooling of initially liquid crystallohydrate core droplets during preparation of energy nanocontainers.

DSC results demonstrated high thermal stability of nanoencapsulated single and mixed crystallohydrates, which remained unchanged after 100 thermal cycles (Figure 9). Encapsulation of the crystallohydrate mixtures also reduced supercooling (Figure 9c, d). Encapsulated 1:2 % wt. Mg(NO$_3$)$_2$·6H$_2$O:Na$_2$SO$_4$·10H$_2$O eutectic mixture has one well defined phase transition peak with T_M = 15.4°C and T_F = -1.1°C. The transition is stable over >100 heat uptake/release cycles and has latent heat capacity of 126.8 J·g^{-1}, which showed 67% encapsulation efficiency. Additive mixtures of crystallohydrate-loaded nanocontainers have high potential to design multi-temperature heat storage systems containing energy nanocontainers with different PCM cores sensitive to different transition temperatures.
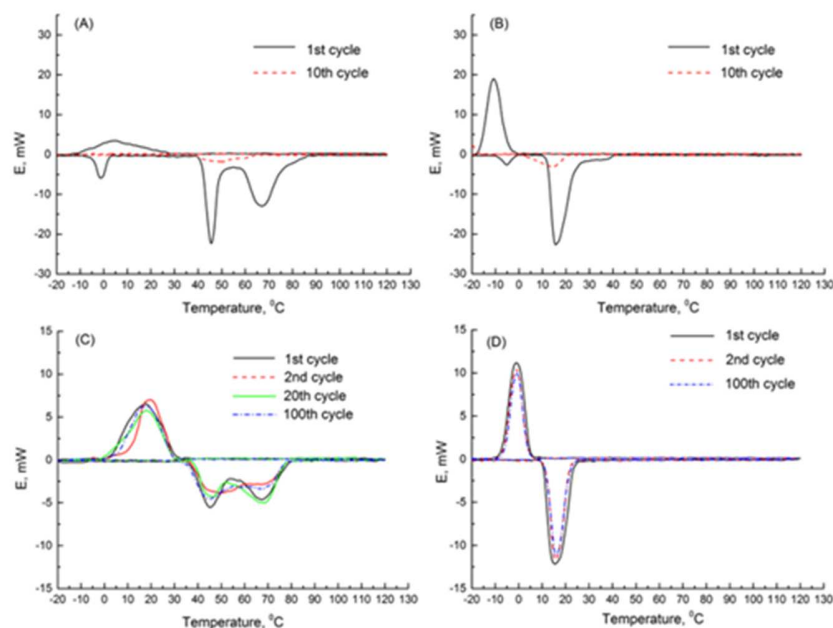
Figure 9. DSC data for (A) 1:1 % wt. $Mg(NO_3)_2 \cdot 6H_2O:Na_2SO_4 \cdot 10H_2O$ bulk mixture, (B) 1:2 % wt. $Mg(NO_3)_2 \cdot 6H_2O:Na_2SO_4 \cdot 10H_2O$ bulk mixture, encapsulated 1:1 % wt. $Mg(NO_3)_2 \cdot 6H_2O:Na_2SO_4 \cdot 10H_2O$ and encapsulated 1:2 % wt. $Mg(NO_3)_2 \cdot 6H_2O:Na_2SO_4 \cdot 10H_2O$.[62]

Huang *et al.* used $Na_2PO_4 \cdot 12H_2O$ as core material and methyl methacrylate as monomer along with ethyl acrylate as crosslinker.[63] The shell was made by a suspension polymerisation combined with solvent evaporation. They found that upon encapsulation the PCM was partially dehydrated to form $Na_2PO_4 \cdot 7H_2O$ which resulted in an increase in melting temperature from 36°C to 51°C. Importantly, upon encapsulation the thermal conductivity increased from 1.01 $W \cdot m^{-1}K^{-1}$ for pure $Na_2PO_4 \cdot 12H_2O$ to 1.426 $W \cdot m^{-1}K^{-1}$ for the encapsulated $Na_2PO_4 \cdot 7H_2O$. Platte *et al.* encapsulated different mixtures of sodium sulphate, sodium phosphate and sodium carbonate that were hydrated by dissolving in water and the shell was formed by a surface-thiol Michael addition polymerisation.[64] Schoth *et al.* developed a surfactant free method to

encapsulate sodium sulphate decahydrate.[65] They utilised the Pickering emulsion technique to create the initial emulsion. It was shown that $Na_2SO_4\cdot10H_2O$ could be encapsulated up to 20 % wt., which is its solubility limit in water. Strong interface interactions between core and shell materials can influence on the heat uptake/release of the capsules, similar to that observed for encapsulation of organic PCMs.[66] Relatively large specific surface area of the encapsulated crystallohydrates accelerates nucleation of hydrated salts, leading to reduction of subcooling.[67]

CONCLUSIONS&OUTLOOK

The research on the nanocontainer-based active coatings was started in 2005 in the Department of Interfaces, Max Planck Institute of Colloids and Interfaces under the guidance of Prof. Helmuth Möhwald. Since that time, this topic attracted considerable attention across the scientific world with >1500 publications during last decade. This approach is very versatile and can be applied not only for autonomous self-healing coatings but also for other multifunctional responsive materials.

The main advantage of self-healing coatings is their autonomic response to the corrosion or any other defects in the coating. After the damage is terminated, the release of the encapsulated active agents stops and coating restores its characteristics. The current main challenge is the transfer of the research achievements in the self-healing coatings to the commercialisation level. This research work requires close collaboration with paint producers to adapt developed nanocontainers to the commercial paint formulations and pass all industrial test requirements.

Another great opportunity is to extend self-healing approach to the multifunctional nanocontainers able to encapsulate several active materials and respond to different triggering

impacts. This can attain the bulk systems additional functionality (like demonstrated antifouling or thermo-regulating) responding to the various environmental changes. Many efforts have to be done here, mostly focusing on the mechanisms of bulk matrix-shell and nanocontainer-nanocontainer interactions.

AUTHOR INFORMATION

Corresponding Author

*Prof. Dmitry Shchukin, Stephenson Institute for Renewable Energy, Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD, Liverpool, UK. E-mail: d.shchukin@liverpool.ac.uk.

Dr. Elena Shchukina received PhD in Organic Chemistry at the Belarussian Academy of Sciences, Belarus. She has gained experience in organic chemistry working in different industries. Since 2015, she is project leader in Stephenson Institute for Renewable Energy, University of Liverpool, working on the encapsulation of active materials for self-healing and thermal energy storage.

Prof. Dmitry Shchukin was a group leader at the Department of Interfaces, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany, in 2007-2012. He obtained his PhD (2002) in physical chemistry. Currently, he is Professor in Chemistry, Stephenson Institute for Renewable Energy, University of Liverpool and Director of University's Ultra Mixing and Processing Facility (UMPF). His main research expertise is encapsulation of active materials and chemistry at cavitation interface.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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