coatings

Editorial

Special Issue: Corrosion Effects and Smart Coatings of Corrosion Protection

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Citation: Zhao, X.; Jiang, D.; Ma, L.; Zeng, X.; Li, Z.; Huang, G. Special Issue: Corrosion Effects and Smart Coatings of Corrosion Protection. *Coatings* **2022**, *12*, 1378. https://doi.org/10.3390/coatings12101378

Received: 13 September 2022
Accepted: 15 September 2022
Published: 21 September 2022

Materials that are capable of adapting their properties dynamically to an external stimulus are called stimuli-responsive or "smart materials" [1]. The development of intelligent coatings (smart coatings) originates from the research of intelligent materials. Hence, smart coating is a coating which detects and responds dynamically to the changes in its environment in a functional and predictable manner [2]. Compared with traditional organic coatings, which have better corrosion and pollution resistance [3], there are now many types of intelligent coatings, such as coatings that are self-healing, self-reporting, antibacterial, and so on. Ni et al. [4] mixed mesoporous polydopamine microspheres with aqueous epoxy resin and hydrophobic silica nanoparticles to prepare a self-healing intelligent antifouling coating. Under the stimulation of the external environment, the defects in the coating can be self-healed, and the superhydrophobic and antifouling properties of the coating can be restored. Wang et al. [5] designed a stimulus-responsive mesoporous silica nano-container loaded with fluorescein isothiocyanate and added it to the epoxy coating. Through the change in the corrosion environment at the damaged part, the fluorescent probe molecules were stimulated to release fluorescence, so as to realize the self-report function of the coating. Xu et al. [6] linked poly(2-diisopropylaminoethyl methacrylate)-b-poly(2-methacryloyloxyethyl phosphate choline) (PDPA-b-PMPC) and poly lysine (plys) on tannic acid (TA) to prepare an intelligent antibacterial coating, which showed significant antibacterial activity and adsorption to proteins. On the basis of passive barrier, these coatings achieve active protection by responding to changes in the external environment and improve the service life of the coatings [7].

Many so-called smart coatings that do not respond to changes in a dynamic and reversible manner may actually be classified as very-high-performance and novel coatings. Smart coatings can be designed and prepared in many ways such as by incorporating stimuli-responsive materials such as light, pH, pressure, temperature, etc., sensitive molecules, nanoparticles, and antimicrobial agents as additives [8]. Loading the corrosion inhibitor and the healing agent into the micro–nano-container and realizing the release of their stimulus response in the coating are conducive to maintain their long-term reactivity and stability. Leal et al. [9] synthesized microcapsules containing linseed oil and then added benzimidazole between microcapsules and pH-responsive polyelectrolyte Pei layer by layer self-assembly technology to prepare a new smart coating of stimulus responsive microcapsules and proved the anti-corrosion performance of epoxy coating containing microcapsules by electrochemical impedance spectroscopy (EIS). Cao et al. [10] synthesized pH-responsive polyaniline hollow microspheres encapsulating corrosion inhibitor 2-Mercaptobenzothiazole and combined them with aqueous epoxy resin to prepare intelligent coatings, which have excellent corrosion resistance and self-healing ability. Liu et al. [11] successfully prepared environmentally friendly pH-sensitive mesoporous chitosan microspheres by W/O lotion chemical crosslinking method and added them to polyacrylate coating. The self-healing performance of the coating is improved, and the further expansion of corrosion is prevented due to the release of corrosion inhibitors. According to the electrochemical impedance spectrum, the release rate of the inhibitor is the fastest at pH = 9. Wang et al. [12] modified mesoporous silica by 2-Diethylaminoethyl methacrylate (DEAEMA) and loaded the corrosion inhibitor benzotriazole (BTA) in the nanocontainer to prepare pH responsive nanocontainers. The pH-responsive epoxy composite coating was obtained by adding the nanocontainers to the epoxy coating.

Duan et al. [13] synthesized ZIF-8, which can explain the release of corrosion inhibitor in acidic water, by a microemulsion method, and studied the protective performance of different mass fractions of ZIF-8 on epoxy coating. The results show that the anti-corrosion performance of the modified epoxy coating is improved with the increase in the mass fraction of ZIF-8 filler. In addition, the author also pointed out that the excellent anti-corrosion performance of ZIF-8 coating may be attributed to two reasons. First, ZIF-8 as a nano filler can block the micropores generated during the preparation and curing of the coating and reduce the penetration path of corrosive electrolyte solution; secondly, the amine group in ZIF-8 reacts with the epoxy group, which not only increases the crosslinking density of the coating but also improves the dispersion of ZIF-8 in the coating. ZIF-7 has similar performance to ZIF-8, which can hydrolyze and release corrosion inhibitor under acidic conditions. Yang et al. [14] studied the anti-corrosion performance of ZIF-7 and the influence of the content and size of ZIF-7 on the coating performance. The electrochemical impedance changes in the epoxy coating added with ZIF-7 and the blank epoxy coating in HCl solution were compared. The results showed that the epoxy coating added with ZIF-7 showed a good corrosion inhibition effect on the steel substrate in acidic medium. When the content of ZIF-7 was 1.7 wt.%, the corrosion resistance of the coating was the best. On the basis of Yang et al., Guo et al. [15] prepared BTA@ZIF-7 nanoparticles under acidic conditions. The inhibition efficiency of nanoparticles can be as high as 99.9%, and the release amount of corrosion inhibitor can reach 30 wt.% within 10 min, while the release amount of corrosion inhibitor is less than 4 wt.% under neutral conditions. Electrochemical impedance spectroscopy indicates that coatings containing BTA@ZIF-7 are impedance modulus at low frequency volumes up to $1.86 \times 10^5\ \Omega\cdot cm^2$.

In addition to the pH-responsive intelligent anti-corrosion coating, there are also temperature responsive intelligent anti-corrosion coatings. Li et al. [16] designed a new nano container composed of hollow silica inner wall and stimulus responsive polymer outer wall. When *N*-isopropylacrylamide is selected as the polymer, the nanocarrier responds to temperature, thus achieving the controllable release of benzotriazole (BTA), a corrosion inhibitor.

Photoresponsive self-healing coatings have the advantages of the instantaneous, remote, environmental protection, and accurate repair of damaged parts. Chen et al. [17] used silica microspheres as templates to prepare hollow mesoporous silica microspheres and used azobenzene isomers to modify the inner wall of the mesoporous to obtain photoresponsive hollow mesoporous nanocarriers. The photoresponsive nanocarriers can release corrosion inhibitors under ultraviolet light and inhibit the diffusion of corrosion inhibitors under visible light, realizing the controllable release of photoresponsive corrosion inhibitors.

Stimuli-responsive materials are combined with superhydrophobic materials and antifouling agents, which can achieve controllable release of antifouling agents. Chen et al. [18] modified ZIF-8 nanoparticles with low-surface-energy materials 1H,1H,2H,2H-perfluorooctyltriethoxysilane and prepared a superhydrophobic coating with epoxy resin as binder. According to electrochemical impedance spectroscopy, it was found that at 3.5 wt.% after soaking in NaCl solution for 1 h, the charge transfer resistance of Q235 steel was increased by more than seven orders of magnitude, while the impedance modulus at low frequency decreased by less than one order of magnitude after soaking for 7 days. The excellent self-cleaning ability of the coating was proved by the dripping test and immersion test, which indicated the anti-corrosion performance of the superhydrophobic coating. Hao et al. [19] prepared intelligent bacteria-triggered multilayer films by adding pH-responsive chitosan nanocapsules to control the release of antifouling agents during bacterial growth. Chitosan and capsaicin (CAP) combine to form nanocapsules to achieve pH-responsive behavior. The electrostatic interaction between algal salt (ALG) and polydopamine (PDA) in solution leads to (PDA/Alg-CAP@CS-n). After the M membrane was scratched mechanically in artificial seawater solution, it showed self-repairing behavior due to the penetration of ions and the transfer of free chains. The design of multilayer films provides a new idea for the research of antifouling agents in the field of controlled release, and the self-healing performance can further extend its service life in the field of antifouling.

Adding a color indicator or a fluorescent indicator corresponding to pH to the coating can also realize self-warning of the coating [20]. Maia et al. [21] encapsulated the pH indicator phenolphthalein (PHPH) into polyurea microcapsules, which has ideal compatibility with polyurethane coatings. When the metal substrate is corroded, the oxygen molecules in the cathode area obtain electrons and react with water to generate OH^-, which increases the pH value of the cathode area, and phenolphthalein turns pink to indicate the occurrence of corrosion. Wang et al. [22] loaded benzotriazole (BTA) and fluorescent molecular probe coumarin into pH-responsive polymer microspheres, pdvb-graft-p (DVB co AA), and then dispersed them in epoxy resin coating to prepare an intelligent coating with self-warning and self-healing functions. The intelligent coating can provide timely fluorescent self-warning at the damage site of the coating on the surface of carbon steel, copper alloy, aluminum alloy, and other metals and prevent the occurrence and spread of corrosion at the damaged part of the coating. It also has good self-warning and self-healing functions for the damage caused by fatigue fracture of the coating.

In addition, smart coatings can also strategically design polymer structures and coatings that respond to internal or external stimuli. This type of intelligent coating mainly relies on external stimuli such as temperature and light to trigger a series of physical and chemical reactions to repair the coating. Temperature stimuli are the most common trigger conditions. At present, most of the temperature-responsive self-repairing is realized through the thermally reversible reaction of crosslinked linear polymers, especially the Diels–Alder (DA) reaction [23]. Fang et al. [24] prepared a self-healing polyurethane (PU) network based on reversible DA reaction between anthracyl and maleimide groups. When the coating cracks, in order to consume crack energy, DA products at the crack decompose to form free anthracene and maleimide. Then, these cracks are heated. The initial stage of heating causes the material to expand, and the polymers on both sides of the cracks are in close contact with each other. Hydrogen bonds and molecules are rearranged. After heating, the DA reaction of the decomposition product occurred again, and a new DA bond was established. Therefore, the network structure of the polymer is restored and the cracks are healed. Fan et al. [25] prepared a shape-memory polyurethane self-healing coating, which was mixed with microcapsules loaded with Alodine 5200 inhibitor and heating agent. An automatic induction heating mechanism is introduced in the self-healing process. When the coating is damaged, the inhibitor released by the microcapsule reacts with the aluminum alloy matrix. A passivation film is formed at the bottom of the scratch. At the same time, the released heating agent reacts with oxygen to generate a large amount of heat and promote the healing of Shape-memory polymer (SMP). The experimental results show that the introduction of automatic induction heating into shape memory polyurethane can effectively improve the self-healing performance and corrosion resistance of the coating.

In a word, there could be thousands of systems that could be used to fabricate smart coatings. It is very important to find a system that can efficiently respond to stimuli to realize industrial application. Towards this goal, we are assembling a Special Issue on smart coatings to encourage researchers and to provide them with a platform to publish their novel studies as well as to enhance the smart coatings for application in corrosion protection, early detection, dangerous alarming, and in situ repairing.

The theme of this Special Issue broadly includes (but is not limited to):

- stimuli-responsive coatings;
- antimicrobial coatings;
- antifouling coatings;

- conductive coatings;
- self-healing coatings;
- super hydrophobic systems.

Author Contributions: Conceptualization, L.M.; methodology, D.J.; investigation, G.H.; writing—original draft preparation, G.H.; writing—review and editing, G.H.; supervision, X.Z. (Xian Zeng); finding literature, X.Z. (Xiaoshuo Zhao) and Z.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Foundation of State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, grant number SLS 2018.

Acknowledgments: The authors thanks to Xudong Sui for providing anti-abrasive test condition. The authors thanks to Qingjun Chen for providing FAA powders.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wieszczycka, K.; Staszak, K.; Woźniak-Budych, M.J.; Litowczenko, J.; Maciejewska, B.M.; Jurga, S. Surface functionalization—The way for advanced applications of smart materials. *Coord. Chem. Rev.* **2021**, *436*, 213846. [CrossRef]
2. Nazeer, A.A.; Madkour, M. Potential use of smart coatings for corrosion protection of metals and alloys: A review. *J. Mol. Liq.* **2018**, *253*, 11–22. [CrossRef]
3. Thomas, D.; Philip, E.; Sindhu, R.; Ulaeto, S.B.; Pugazhendhi, A.; Awasthi, M.K. Developments in smart organic coatings for anticorrosion applications: A review. *Biomass Convers. Biorefinery* **2022**, 1–17. [CrossRef]
4. Ni, X.; Gao, Y.; Zhang, X.; Lei, Y.; Sun, G.; You, B. An Eco-Friendly Smart Self-Healing Coating with NIR and PH Du-al-Responsive T Superhydrophobic Properties Based on Biomimetic Stimuli-Responsive Mesoporous Polydopamine Microspheres. *Chem. Eng. J.* **2021**, *406*, 126725. [CrossRef]
5. Wang, J.-P.; Song, Y.; Wang, J.-K.; Zhou, Q.; Li, Z.; Han, Y.; Yang, S.; Li, G.L.; Qi, T. PH-Responsive Polymer Coatings for Reporting Early Stages of Metal Corrosion. *Macromol. Mater. Eng.* **2017**, *302*, 1700128. [CrossRef]
6. Xu, G.; Neoh, K.G.; Kang, E.-T.; Teo, S.L.-M. Switchable Antimicrobial and Antifouling Coatings from Tannic Ac-id-Scaffolded Binary Polymer Brushes. *ACS Sustain. Chem. Eng.* **2020**, *8*, 2586–2595. [CrossRef]
7. Cui, G.; Bi, Z.; Wang, S.; Liu, J.; Xing, X.; Li, Z.; Wang, B. A comprehensive review on smart anti-corrosive coatings. *Prog. Org. Coat.* **2020**, *148*, 105821. [CrossRef]
8. Liu, T. Smart Protective Coatings with Self-sensing and Active Corrosion Protection Dual Functionality from PH-Sensitive Calcium Carbonate Microcontainers. *Corros. Sci.* **2022**, *200*, 110254. [CrossRef]
9. Leal, D.A.; Riegel-Vidotti, I.; Ferreira, M.; Marino, C. Smart coating based on double stimuli-responsive microcapsules containing linseed oil and benzotriazole for active corrosion protection. *Corros. Sci.* **2018**, *130*, 56–63. [CrossRef]
10. Cao, Y. Novel Long-Acting Smart Anticorrosion Coating Based on PH-Controlled Release Polyaniline Hollow Microspheres Encapsulating Inhibitor. *J. Mol. Liq.* **2022**, *359*, 119341. [CrossRef]
11. Liu, X.; Li, W.; Wang, W.; Song, L.; Fan, W.; Gao, X.; Xiong, C. Synthesis and Characterization of PH-Responsive Mesopo-rous Chitosan Microspheres Loaded with Sodium Phytate for Smart Water-Based Coatings. *Mater. Corros.* **2018**, *69*, 736–748. [CrossRef]
12. Wang, J.; Yang, H.; Meng, Z.; Xie, B.; Yu, X.; Su, G.; Wang, L. Epoxy Coating with Excellent Anticorrosion and PH-Responsive Performances Based on DEAEMA Modified Mesoporous Silica Nanomaterials. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *634*, 127951. [CrossRef]
13. Duan, S.; Dou, B.; Lin, X.; Zhao, S.; Emori, W.; Pan, J.; Hu, H.; Xiao, H. Influence of active nanofiller ZIF-8 metal-organic framework (MOF) by microemulsion method on anticorrosion of epoxy coatings. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *624*, 126836. [CrossRef]
14. Yang, S.; Wang, J.; Mao, W.; Zhang, D.; Guo, Y.; Song, Y.; Wang, J.-P.; Qi, T.; Li, G.L. PH-Responsive Zeolitic Imidazole Framework Nanoparticles with High Active Inhibitor Content for Self-Healing Anticorrosion Coatings. *Colloids Surf. A Physicochem. Eng. Asp.* **2018**, *555*, 18–26. [CrossRef]
15. Guo, Y.; Wang, J.; Zhang, D.; Qi, T.; Li, G.L. PH-Responsive Self-Healing Anticorrosion Coatings Based on Benzotria-zole-Containing Zeolitic Imidazole Framework. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *561*, 1–8. [CrossRef]
16. Li, G.L.; Zheng, Z.; Möhwald, H.; Shchukin, D.G. Silica/Polymer Double-Walled Hybrid Nanotubes: Synthesis and Application as Stimuli-Responsive Nanocontainers in Self-Healing Coatings. *ACS Nano* **2013**, *7*, 2470–2478. [CrossRef]
17. Chen, T.; Chen, R.; Jin, Z.; Liu, J. Engineering Hollow Mesoporous Silica Nanocontainers with Molecular Switches for Continuous Self-Healing Anticorrosion Coating. *J. Mater. Chem. A* **2015**, *3*, 9510–9516. [CrossRef]
18. Chen, H.; Wang, F.; Fan, H.; Hong, R.; Li, W. Construction of MOF-Based Superhydrophobic Composite Coating with Excellent Abrasion Resistance and Durability for Self-Cleaning, Corrosion Resistance, Anti-Icing, and Loading-Increasing Research. *Chem. Eng. J.* **2021**, *408*, 127343. [CrossRef]

19. Hao, X.; Wang, W.; Yang, Z.; Yue, L.; Sun, H.; Wang, H.; Guo, Z.; Cheng, F.; Chen, S. PH Responsive Antifouling and Antibacterial Multilayer Films with Self-Healing Performance. *Chem. Eng. J.* **2019**, *356*, 130–141. [CrossRef]
20. Ma, L.; Ren, C.; Wang, J.; Liu, T.; Yang, H.; Wang, Y.; Huang, Y.; Zhang, D. Self-Reporting Coatings for Autonomous Detection of Coating Damage and Metal Corrosion: A Review. *Chem. Eng. J.* **2021**, *421*, 127854. [CrossRef]
21. Maia, F.; Tedim, J.; Bastos, A.C.; Ferreira, M.G.S.; Zheludkevich, M.L. Active Sensing Coating for Early Detection of Corrosion Processes. *RSC Adv.* **2014**, *4*, 17780. [CrossRef]
22. Wang, J.-P.; Wang, J.-K.; Zhou, Q.; Li, Z.; Han, Y.; Song, Y.; Yang, S.; Song, X.; Qi, T.; Möhwald, H.; et al. Adaptive Poly-meric Coatings with Self-Reporting and Self-Healing Dual Functions from Porous Core-Shell Nanostructures. *Macromol. Mater. Eng.* **2018**, *303*, 1700616. [CrossRef]
23. Kötteritzsch, J.; Stumpf, S.; Hoeppener, S.; Vitz, J.; Hager, M.D.; Schubert, U. One-Component Intrinsic Self-Healing Coatings Based on Reversible Crosslinking by Diels-Alder Cycloadditions. *Macromol. Chem. Phys.* **2013**, *214*, 1636–1649. [CrossRef]
24. Fang, Y.; Li, J.; Du, X.; Du, Z.; Cheng, X.; Wang, H. Thermal- and mechanical-responsive polyurethane elastomers with self-healing, mechanical-reinforced, and thermal-stable capabilities. *Polymer* **2018**, *158*, 166–175. [CrossRef]
25. Fan, W.; Zhang, Y.; Li, W.; Wang, W.; Zhao, X.; Song, L. Multi-level self-healing ability of shape memory polyurethane coating with microcapsules by induction heating. *Chem. Eng. J.* **2019**, *368*, 1033–1044. [CrossRef]