State of The Art on Development of Superhydrophobic Coatings for Corrosion in Marine Applications

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Abstract. Owing to the water-repellence and anti-sticking properties, superhydrophobic technology has become a burgeoning subject of research area in innumerable fields. A great deal of literature articles covering corrosion control applications has been published. Howbeit, specific review focusing on superhydrophobic approach to ameliorate durability performance of coatings for corrosion protection in marine applications is still lacking. This literature first introduces the basic principles of superhydrophobicity, followed by the discussion of established approaches to fabricate superhydrophobic coatings. Besides that, the recent progress of superhydrophobic coatings intended for marine applications are also discussed. In addition, the challenges and future perspectives of anticorrosion coating for marine applications are presented. As a matter of fact, corrosion in marine environment is undeniably complex due to the diversity of seawater chemistry and the existence of biological organisms living in the ocean. Hence, this review served as ‘food for thought’ on the development of superhydrophobic coating by merging the coatings’ main features including corrosion protection and fouling mitigation in order to improve its sustainability and durability performance in the marine environment.

1. Introduction

Coatings play important role as a remedy to solve metal corrosion. Anti-corrosion is described as the protection of metal surface against corrosive attacks [1]. Chromate-based coatings such as primers and pigments have been the most effective corrosion protection system used conventionally over the years [2]. However, due to environmental and human health concerns, the current legislation passed by Registration, Evaluation and Authorization and Restriction of Chemicals (REACH) has restricted the future usage of dangerous compounds e.g. hazardous air pollutant (HAPs), volatile organic compounds (VOCs) and the hexavalent chromium in most of the sectors and industries [3]. Furthermore, cost-effectiveness remains the key priority in the industrial point of view, but in timeliness, sustainability deliberately became a considered measure [4, 5]. This consequently yields greater support and in development of chromate-free coatings [6]. Throughout the years, different alternatives have been proposed and carried out, such as the smart and green coatings [2]. The applications of smart coatings, such as self-cleaning, self-healing and superhydrophobic coatings are promising routes in future development of high-performance anticorrosive coatings for a broad spectrum of sectors.
2. Superhydrophobic Anticorrosive Coatings

Current trend in corrosion protection efforts began to incline towards superhydrophobic technology to a great extent. This well-known superhydrophobic technology has attracted the research community to pursue in development and discovery of potential superhydrophobic coatings as new materials for corrosion protection in seawater environment [7], owing to its effective control to the corrosion due to its inherent water-repellent nature [8]. Over the years, intense research has been devoted to the anticorrosion and antifouling properties of superhydrophobic coatings [9-14].

2.1. Introduction About Superhydrophobicity

The development of superhydrophobicity is inspired by nature, e.g. ‘the lotus effect’, a well-known natural phenomenon discovered by Barthlott and Ehler in the late 1970s [15]. They observed that the lotus plant, which grows in a muddy water, has leaves that are always perfectly clean, due to its ability to clean itself of dirt. This is due to the unique surface structure of lotus leaf and the presence of low surface energy on its surface [16]. These features create superhydrophobicity on the lotus leaf’s surface, allowing the water droplets to roll over without any wetting effect [17]. The superhydrophobic surfaces can also be found in some other plants and animals and this allowed them to survive better in their environment. For examples, mosquitoes’ eyes serve for antifogging, planthopper wing for antibacterial, legume Melilotussiculus with leaves that can separate itself from the seawater etc. [18, 19].

Technically, superhydrophobic is termed as surface with water contact angle above 150° [7, 20]. Superhydrophobic surface can be obtained by employing technology to modify the roughness and surface energy to develop a topography with self-cleaning ability [7]. The role of roughness with hierarchical micro- or nanoscale is to trap air on the surface and increases the surface’s water contact angle, whereas the low surface energy helps to weaken the bonding between water and the surface. The fundamental principles of superhydrophobic materials can be explained in terms of four major aspects: (1) wetting, (2) contact angle, (3) surface roughness, and (4) surface energy [21].

2.1.1. Wetting

In fact, wettability indicates the liquid’s behaviour on the studied surface. When liquid molecules have higher tendency to interact with solid surface rather than the liquid, they will spread on the solid surface. This phenomenon is known as wetting [21]. Wetting occurs only when the free energy of the system is low. Thus, the lower the free energy, the better the wettability. On a superhydrophobic surface, in comparison with the solid surface, the liquid molecules have higher tendency to interact with each other. As followed by the wetting does not occur, the liquid tends to condense to spherical forms. This denoted the non-wetting behaviour as a distinctive feature of superhydrophobic surface.

2.1.2. Contact Angle

The quantitative indicator of wettability is represented by the contact angle (CA). CA is described as the angle between the surface of the liquid and the outline of the contact surface. The wetting behaviour of a surface is considered superhydrophobic surface if CA ranged 150°<\theta\leq180°. In CA analysis, commonly tensiometer is used to measure the droplet of liquid which is dropped onto solid surface with a micro-syringe [21].

2.1.3. Surface Roughness

To achieve superhydrophobic surface, the surface must have hierarchical micro or nano-roughness and morphology. Several researchers have correlated the influence of surface roughness of the hierarchical structures to the contact angle of water droplet on the surface with the wetting modes of Cassie-Baxter and Wenzel’s [22].

2.1.4. Surface Energy

Molecules of liquids and solid at surfaces do not have similar atmosphere as volume, they have connection with lesser molecules compared with molecules in bulk phase. They have higher potential
energy on the surface because there are few chemical bonds present on the surface. This energy of surface molecules is called surface energy. The result of surface energy of the solid depends on the liquid. If molecules of solid and liquid are contacted with each other directly, the surface energy will be lower. Low surface energy surface will reduce the ability of water to bond with the surface.

2.2. Development of superhydrophobic anticorrosive coatings
In order to ensure the long-term durability of the equipment, both selection of material and fabrication method to form a superhydrophobic coating should be considered wisely. The process conditions, structural properties and the possible changes that can happen during the processing have to be overlooked. A good anticorrosive coating exhibits a few properties such as good barrier properties, good appearance, and cost-effective. In general, the water contact angle analysis is used as a criterion to evaluate the hydrophobicity of a surface. To evaluate the corrosion, it can be determined by several parameters including open circuit potential, polarization resistance and corrosion rate. Besides corrosion evaluation, some other properties are also vital to complete the performance of an anticorrosive coating and they can be evaluated by: surface energy test, water absorption test, adhesion properties, scratch test, abrasion test, mechanical indentation etc. [23]

With the fast pace of technology advancement, variety kinds of techniques have been explored to fabricate superhydrophobic coating, whether by mechanical, electrochemical, thermal or chemical means. The selection of technique used depends specifically on the material applications and properties desired of the coating. Commonly, superhydrophobic surfaces can be achieved with two key strategies [24]. First, by creating rough structure on a hydrophobic surface which has contact angle more than 90°. And the other is by modifying the rough surface with a low surface energy material. It is often first considered to modify the surface with low surface energy material, e.g. fatty acid or silane-based polymer [25, 26]. However, these smooth hydrophobic surfaces usually showed water contact angle that hardly exceeds 120° [27]. Introducing rough structures to these surfaces can help them to reach superhydrophobic state, with water contact angle exceeding 150°.

3. State-Of-Art of Superhydrophobic Anticorrosive Coatings for Marine Applications
Corrosion condition in marine environment is undeniably complex as there are multiple potential factors influencing corrosion in seawater, due to the existence of marine biodiversity including microorganisms, plants and animals living in the marine setting [23]. Besides that, it is critical to note that fouling is also a significant factor influencing corrosion in marine environment. The formation of unwanted deposited on the metal components during their interaction with sea water often lead to both corrosion and biofouling issues. Without doubt, coatings for corrosion protection in marine require a combination of properties such as good anticorrosion, fouling resistance, good adhesion to substrate, good barrier and compatibility with other components in the protective system. For few decades, fluorine-based biocides, e.g. tributyltin have been incorporated with the marine paints due to their effectiveness in fouling resistance and protection of ship hulls [28, 29]. However, accumulation of these toxic chemicals in seawater led to negative impacts to the ecosystems, consequently constrained their usage in marine industries [2]. Thus, with the demand of technological needs, there is a growing interest in corrosion-protection coatings with antifouling mechanisms [30]. In this sense, superhydrophobic coatings particularly became an attractive candidate in this research area.

Owing to the water-repelling and anti-sticking properties of superhydrophobic surface, it becomes a promising strategy for enhancing corrosion resistance and biofouling mitigation, because of its capability in inhibiting any water or environmental cause to direct contact with the metal substrates. Over decades, superhydrophobic coatings with anticorrosion or antifouling function in marine applications have been extensively studied respectively[10]. However, the assessment of combined properties in a coating system with superhydrophobic approach is rarely reported [2]. Table 1 depicted the collection of articles reported on coatings with combined properties of anticorrosion and marine fouling inhibition implementing superhydrophobic approach. They credited the improvement in corrosion resistance is attributed by the entrapment of air cushion layer between the rough surface
structure, allowing water droplet to contact in Cassie’s mode. Besides that, the fouling resistance phenomena can be explained by the contribution of low adhesion and lotus effect of superhydrophobic surface resulted in slippery effect against the fouling’s settlement.

Table 1. Superhydrophobic coatings with combined properties of anticorrosion and antifouling.

| Substrate | Coating Material | Fabrication method | Source |
|-----------|-----------------|-------------------|--------|
| aluminium (Al) | manganese stearate | electrodeposition + stearic acid surface modification | [31] |
| carbon (C) | silica ormosil / polymethylhydroxysiloxane (PMHOS) | self-assembly of nanoparticles and surface modification by different fluorosilane molecules | [32] |
| Al | Dianthus caryophyllus-on-nanowires | high speed hard anodization and surface modification by 1H, 1H, 2H, 2H perfluorodecyldriethoxysilane | [33] |
| Al | polyaniline (PANI)/chitosan/zinc stearate | Polymerization of PANI and electrodeposition of chitosan and zinc stearate | [34] |
| Copper zinc | Dodecanethiol modified Cu (OH)₂ bundle cluster | Electrodeposition-oxidation and surface modification using dodecanethiol | [35] |
| Aluminum alloy (AA) 5083 | ammonia etched PFDTES modified micro-nano texture superhydrophobic surface | ammonia etching and surface modification | [36] |
| AZ31B magnesium alloy | Stearic acid modified MnO₂ | in situ immersion in MnSO₄ solution and stearic acid surface modification | [37] |
| Steel | nano-magnetite and silicone dispersed in linear dihydroxy r ã, õ-dihydroxy-polydimethylsiloxane (PDMS) | Solution casting | [38] |
| high strength low-alloyed steel | SiO₂ and Cu₂O nanoparticles functionalized PEO/TSA | plasma electrolytic oxidation on TSA and functionalization with nanoparticles (on topcoat). | [39] |
| AZ31 | tetradecanoic acid iron (Fe(CH₃(CH₂)₁₂COO)₃) | Immersion in ferric chloride (FeCl₃·6H₂O), deionized water, tetradecanoic acid (CH₃(CH₂)₁₂COOH) and ethanol | [40] |

4. Challenges and Future Trends in Development of Superhydrophobic Coating to Solve Corrosion Issues in Marine Environment

Based on the records of publications and reviews over the years, it was no doubt that the development of superhydrophobic technology has received tremendous interests in marine coating industry owing to the capability of superhydrophobic coatings to achieve greater corrosion protection. However, the lack of sustainability and stability of these coatings has discouraged its practical applications, not to mention the need to be exposed to the aggressive conditions in marine environment. Although several strategies of superhydrophobic coatings for anticorrosion in marine environment have been published, there is still lack of solutions based on fouling mitigating approach in anticorrosion coatings. The merging of these functionalities is meaningful as it adds values and provides greater effectiveness to solve corrosion problems in marine environment as they are capable to confront different attacks simultaneously [2].
Superhydrophobic coating does not only able to repel corrosion but they also minimize the adhesion of bacteria to the metal, and easy removal of bacteria [41]. To realize its practical applications, there is a need to validate their potential in real marine environment.

Besides that, superhydrophobic coatings that are lack of stability after long term exposure will lose efficiency in bacterial attachment inhibition and lead to easier formation of biofilm on the coatings [42]. Thus, retaining mechanical stability of these superhydrophobic structures is as important as achieving higher superhydrophobicity [20]. The fabrication technique of the superhydrophobic coating may influence its native stability [43]. Other influencing factors, including adhesion strength of the coating to the substrate [44], abrasive resistance of the coating material [45] and the dynamic impact resistance of the coating material [46] are also important parameters determining the overall mechanical stability of a superhydrophobic coating. Interfacial strength within the components of matrix including nanostructures, binding materials and substrate is an important factor influencing the mechanical stability of superhydrophobic structures [27].

As the world today is concerning of what is discharged into the environment, and thus development of the environmental legislations. Sustainability deliberately became a considered measure in the industrial point of views, even though cost-effectiveness remains the priority [4, 5, 47]. Combating environmental problems with the utilization of eco-friendly materials are not enough, but their effects of the applications also need to be taken care of. Besides that, there is a need to design green superhydrophobic coatings with effective anticorrosion and antifouling properties with sustainable and environmental-friendly materials. This approach could give merits including: (a) result in lower or zero environmental impact; (b) minimizing toxicity proportion; (c) from preparation of raw materials to processing and application is a new cost effective alternate to replace the conventional products.

5. Conclusion
Different strategies have recognized the improvement of superhydrophobicity on the properties corrosion inhibition and marine fouling mitigation to prolong the performance of different metals that are commonly used in marine, as superhydrophobic coating, which has contact angle greater than 150° is capable to act as barrier to protect metal interface and delay onset of corrosion by blocking the diffusion of any corrosive species, or event fouling agents across the metal surface through the coating. Moreover, merging two functionalities: corrosion inhibition and marine fouling mitigation makes superhydrophobic coatings a promising potential in marine applications.

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