A perspective on nanocomposite coatings for advanced functional applications

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Abstract: Functional coatings provide durability to the bulk material and add other value-added properties which enhance the surface's mechanical, electrical, optical, and many other properties. The functional response of these coatings stems from the ambiance, which can be made to sense in response to a sharp change in the temperature, pH, moisture, active ions, or mechanical stresses. Recently, many efforts have been made to impart multi-functionality within a single coating, i.e., to achieve hydrophobicity and antifouling characteristics, which can be achieved by combining an appropriate coating material with a geometric nanopattern. Such coatings are poised to shape the future of the transport, healthcare, and energy sectors, including marine, aeronautics, automobile, petrochemical, biomedical, electrical and electronic industries. This perspective sheds light on the design specifications and requirements to fabricate functional coatings and critically discusses the fabrication methods, working principles, and case studies to survey various applications with a particular focus on anti-corrosion and self-cleaning applications.

Keywords: Nanocomposite; Functional coatings; Self-cleaning; Anti-corrosion coatings.

1. INTRODUCTION

Smart composite coatings may be defined as systems that can provide information about physical and chemical attributes such as thickness and defects which can be used for damage prognosis. They are typically able to respond to an external stimulus such as heat, stress, strain, or corrosive environmental factors and to repair themselves during their service life. Research into smart coatings is in the early stages but is rapidly growing. In industries, it has enhanced the growth of paints and their properties, including cleaning (Aliofkhazraei, 2014), scratching and wear resistance (Boissiere, Grosso, Chaumonnot, Nicole, & Sanchez, 2011). Such coatings can be divided into metallic and ceramic nano coatings, which are essentially nanoscale composite materials.

Additionally, nanocomposite coatings have been helpful in reducing biofouling and structural degradation. They are designed to respond to pH, humidity, heat, and other conditions. Their reaction causes the release of a specific amount of inhibitor to repair faults and damage (Fürstner, Barthlott, Neinhuis, & Walzel, 2005; Kendig, Hon, & Warren, 2003). The significant component of remarkable qualities that enhances the filler being inserted in nanocomposite coatings is the presence of the matrix (Muratore, Clarke, Jones, & Voevodin, 2008). Ceramics, metal, or polymers with dimensions larger than

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nanoscale may occasionally be used. Combining two different material compositions into a single covering is to create a new nanocomposite material with unique properties that sets it apart from an individual constituent. The mechanical qualities also improve significantly due to the nanocomposite behaviour, which provides hydrophobicity and corrosion resistance (Fig. 1) (Uhlmann *et al.*, 2006; Zheludkevich, Shchukin, Yasakau, Möhwald, & Ferreira, 2007).



Figure 1. Different properties of nanocomposite coatings.

2. FORMULATION OF VARIOUS TYPES OF SMART NANOCOMPOSITE COATINGS

2.1. Metallic nanocomposite coatings

Metallic nanocomposite coatings are made up of various pure metals such as iron, copper, nickel, tungsten, zinc, cobalt, and others (Verma & Bhattacharya, 2018a). Unalloyed metals may be used in nanocomposite coatings (Santo, Davim, & engineering, 2012) or alloyed to enhance their properties. Since nanoscale materials behave differently than microscale materials in this scenario, improvement is strengthened by using nanosized composites in the coating (Arai, Saito, & Endo, 2010). Such coating can be used in a variety of fields, including the electrical industry, energy production (Verma & Goel, 2022), tubes and sea water condensers (Rajiv, Iyer, Seshadri, & physics, 1995) as well as the automotive and aerospace industries (JAYA Verma, S Nigam, S Sinha, & ARPITA Bhattacharya, 2018).

2.2. Polymeric nanocomposite coatings

Due to their exceptional qualities, polymeric nanocomposite coatings have been helpful in preventing deterioration corrosion. When fillers are incorporated into a polymer, a polymer nanocomposite becomes multi-functional. The primary function of nanofillers in polymer matrixes is typically to increase rigidity, firmness, heat resistance, saturation and specific conductance. The solvent function reduces attack, combustibility and blighting (Aal & A, 2008; Bahrololoom, Sani, & Technology, 2005).

2.3. Waterborne polymer nanocomposites

Waterborne polymer coatings have excellent qualities, are environmentally friendly and offer a thin layer for friction manipulation, are non-toxic, and are easy to clean. By using moisture as a dissolver, the glazing dissipates. Due to its corrosion behaviour, it is blended with nanoparticles like Fe3O4, Fe2O3 and ZnO (Thiemig, Lange, & Bund, 2007). Water-based alkyds coating is economically advantageous and can be sprayed on or submerged materials, making it a typical water-supported coating. The epoxy coating is a deterrent to control the proliferation of aggressive species and protects the outer layer of alloys and metals against corrosion. Additionally, a locking effect is seen because of the increased amount of Fe3O4 nanoparticles in the coating material. This is an enduring barrier between the coating and the metal by lining the microscopic cracks and preventing corrosive ions from penetrating the coated metal surface (Baghery, Farzam, Mousavi, Hosseini, & Technology, 2010).

3. MULTI-RESPONSIVE PROTECTIVE NANOCOMPOSITE COATINGS

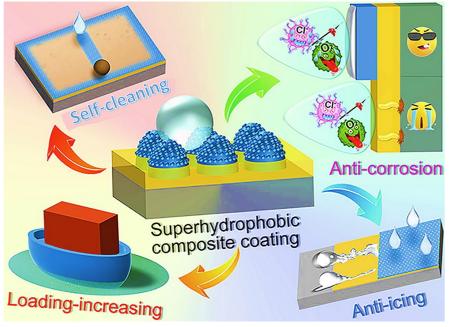
Despite the crucial role that nanotechnology plays in the creation and use of smart coatings, more

research is still necessary to fully nanostructured materials' special properties (Kirthika, Goel, Matthews, & Goel; Verma, Khanna, Sahney, & Bhattacharya, 2020). Smart nanocoatings wrap inhibitor structures with active nanoparticles and functional groups, which enables them to respond intelligently to environmental cues by protecting, mending, absorbing, expelling, or neutering (T. Khaleque & S. Goel, 2022). The military, aerospace, and marine industries use smart coatings the most. For instance, anti-corrosion coatings can detect and stop the deterioration of bioactive nanocoatings like antibacterial coatings (Verma & Bhattacharya, 2018b; Verma et al., 2020). Researchers are currently using a variety of nanocomposites to create multifunctional smart surface coatings, and core-shell structures have proven to be particularly useful in these applications (Fig. 2). Smart coatings using various nanoengineered composite coating types for their multifunctional uses, such as self-cleaning and corrosion resistance, have been reported (Abioye, Musa, Loto, Fayomi, & Gaiya, 2019).

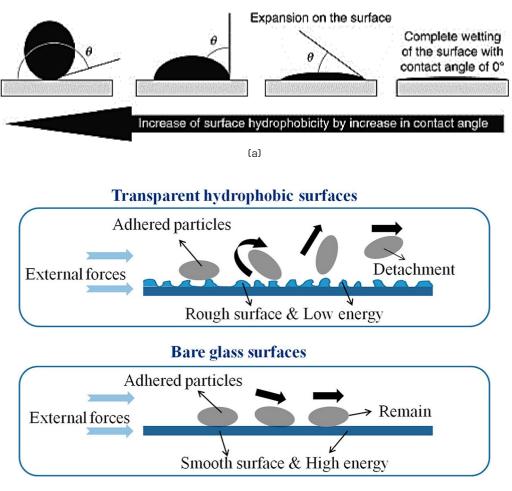
3.1. Hydrophobic self-cleaning coatings

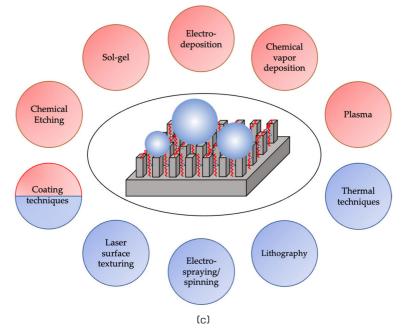
Hydrophobicity that a surface possesses was observed for the first time through the lotus leaf found in nature. It was seen that as water drops on

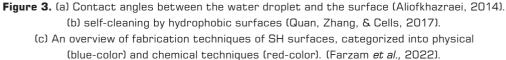




the surface of a lotus leaf, it accumulates in spherical droplets and in slipping from the surface, it removes pollution particles and dirt (Verma, Kumar, & Sikarwar, 2022). The wettability of a solid surface with water in the open air depends on the relationship between water/air, solid/water and solid/ air interface adsorptions. The ratio between these adsorptions is estimated by the contact angle between a water droplet and the surface it is placed on. A contact angle of 0° means complete surface wetting and hydrophilicity, and 180° implies a lack of wetting and complete hydrophobicity (Verma, Baghel, Sikarwar, Bhattacharya, & Avasthi, 2019). As shown in Fig. 3a, contact angles >90° are necessary for a surface to possess hydrophobic effects. As it is impossible to obtain hydrophobic properties with a completely smooth surface, hydrophobic surfaces are developed by adding a rough micro/ nanostructured coating, which causes an increase in the contact angle and a decrease in the surface energy. Thus, micro/nanostructured coating has a low degree of roughness and nanoscale topography (Verma, Nigam, Sinha, Sikarwar, & Bhattacharya, 2017). The more intense the topographies are in the coating, the greater the contact angle, and therefore more water droplets will accumulate. The nano size of the structure prevents pollutants and suspended particles from penetrating the indentions (Fig. 3b). These particles remain on the surface, so the slipping water droplet removes them. The smooth surfaces have a contact angle of 20°. When coated with a silicon resin or fluorocarbon polymer, the contact angle reaches 100° and 110°. To form a good self- cleaning surface, the angle must be at least 160°. Self-cleaning nanocoatings are produced in organic and inorganic forms and are applied by roller print, electrostatic enameling, or spraying techniques to ensure a thin layer (Fig 3c) (Farzam, Beitollahpoor, Solomon, Ashbaugh, & Pesika, 2022).

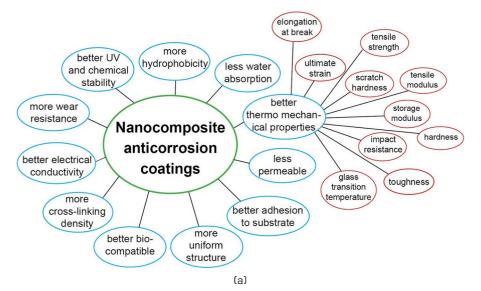






3.2. Nanocomposite smart coatings for corrosion protection

Smart nanocomposite coatings for corrosion protection are appealing because they are one of the most effective, adaptable, affordable and simple techniques on the shop floor. One of the most significant achievements of nanotechnology is using nanocomposites to create anti-corrosion coatings (Fig. 4a) (De Souza & Technology, 2007). It boosts adhesive qualities, anodic and cathodic protection and barrier properties. The creation of smart coatings also uses application as a corrosion inhibitor. Nanoparticles can carry a substantial quantity of corrosive inhibitor particles on their surfaces due to their special characteristics, such as lateral surfaces and high chemical reactivity (He & Shi, 2009).



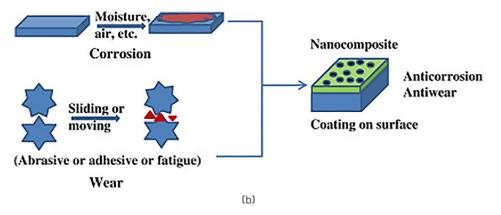


Figure 4. (a) Multifunctionality of anti-corrosion nanocomposite coatings (Nazari *et al.*, 2022) (b) Schematic representation of the concept of nanocomposite coating for anti-corrosion and anti-wear (Kar, 2019).

The main principle in using nanoparticles for smart coatings is the selection of a type which will create tempo-rary bonds with the inhibitors so that the by-products of corrosion are released when these bonds are broken to deliver inhibitors. into the homogeneous medium. In a group of smart anti-corrosion nanocoatings (Al Kiey, Hasanin, & Heakal, 2022; Deyab, El Bali, Mohsen, & Essehli, 2021), the bonds developed between nanoparti-cles and inhibitors are sensitive to the hydroxide ions which are among the main by-products of the metallic corrosion process. As soon as hydroxide ions are released, the bonds are broken. The inhibitor moves toward the damaged area, which is reduced by reacting with the corrosive agents, generating insoluble oxides deposited on the metal surface, preventing electrolytes from diffusing to the metal surface and deactivating it (Fig. 4b) (He & Shi, 2009).

3.2.1. Categories of anti-corrosion coatings

The advantages and drawbacks of protective coatings are outlined in Table 1, along with application tech-niques and levels of protection. There are three main coatings categories: metallic coatings, organic coatings, and inorganic coatings.

(i) Metallic coatings can act as a barrier and provide cathodic protection by galvanically corroding if the metallic coating is less noble than the base metal. Pitting corrosion can happen on the base metal due to flaws if the metallic coating is nobler than the base metal, such as nickel on steel. Hot dipping, electroplating, thermal spraying, cladding, chemical vapour deposition (CVD), and sur-face modification using directed energy (laser or ion) beams are the most used methods for depos-iting metallic coatings (Nazari *et al.*, 2022).

(ii) Inorganic coatings mainly protect the metallic substrate through a barrier protection mechanism; however, inorganic zinc-rich coatings can also provide cathodic protection via the sacrificial activ-ity of zinc. Numerous materials, including hydraulic cement, ceramics, clays, glass, carbon, and sil-icates, are used in inorganic coatings. Chemical conversion coatings are methods for depositing inorganic coatings that may convert the metal surface layer into a passive metal oxide/hydroxide film. It considerably improves the interfacial contacts between the primer coating and the metallic substrate. This conversion layer can be employed as an excellent base for applying protective coatings in addition to its inherent corrosion protection performance. As a result, the organic paint or coating offers superior corrosion resistance and less delamination when used with the conver-sion coating. This procedure can also be used as a cleaning step before painting (Kar, 2019). Ac-cording to a 35year extensive study, inorganic zinc primers outperform organic ones in coastal conditions. Due to the high curing temperature, inorganic sol-gel coatings should not be employed with magnesium or aluminium alloys despite their strong barrier performance. Sol-gel coatings made of an inorganic-organic composite appear to function well because of their flexibility, ability to defend against corrosion, and appropriate curing temperature (Perrin, Ziarelli, & Dupuis, 2020).

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(iii) Organic coatings provide barrier protection and active corrosion inhibition by pigments embed-ded in the coating. Due to the coating's intrinsic permeability to oxygen and water (Olajire, 2018), which limits the barrier characteristics, various fillers are typically added to organic coating com-positions. The anti-corrosion efficacy of organic coatings

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is substantially influenced by the disper-sion state, size, shape, chemical composition, and weight percentage of the filler embedded in the polymeric matrix. Compared to other anti-corrosion treatments, organic coatings, such as paints, varnishes, lacquers, and similar coatings, protect the most metal per tonne (Verma, Gupta, & Kumar, 2022).

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Corrosion protection coatings	Materials used in coatings	Coating techniques	Mechanism of action	Advantages	Disadvantages
Metallic coatings	Cu, Ni, Cr, Zn, Cd, Sn, Au, Ag, Pd, Pt, and etc. in their pure or alloy form	Electroplating, Electroless plating, Hot dipping (immersion), Thermal spraying, Cladding, Vacuum deposition (PVD and CVD)	Barrier protection, Sacrificial protection	Superior and longterm corrosion protection, Excellent electrical conductivity, Excellent mechanical properties, Excellent thermal stability, High durability, High brightness, Easy- to-clean, More predictable lifetime, Still operational if damaged	Expensive, Limited color variety, Hazardous toxic, heavy metals
lnorganic coatings	Inorganic chemical conversion coatings (chromate- based, phosphate- based, rare- earth-based, etc.)	Immersion, Spraying, Brushing, Rolling	Barrier protection, Inhibitive protection	Enhance adhesion of the topcoat, Minimize surface oxidation of the substrate, Decrease surface permeability, Self-healing ability, Quick and simple application, Low cost	Prone to crack, Non-uniform coverage, Must be applied along with other types of coatings to provide good corrosion resistance, Usually toxic and carcinogenic
Organic coatings	Thermoplastics (vinyl resins, chlorinated resins, bitumen, and etc.) Thermosets (epoxy resins, phenolic resins, polyurethane resins, etc.) Elastomers (silicones, rubbers, polyurethanes, polyuretanes,	Brushing, Rolling, Spraying, Dip coating, Flow coating, Roller coating	Barrier protection	Excellent chemical stability, High mechanical resistance, Wide color gamut, Cosmetic appearance, Flexible Easy- to-apply, Multifunctional	Low permeability, Difficult lifetime prediction, High content of toxic volatile organic compounds (VOCs), Poor thermal stability, Low conductivity

 Table 1. Application techniques, protection mechanisms, advantages, and disadvantages of anti-corrosion coatings.

4. APPLICATIONS OF SMART NANOCOATINGS

It is possible to envisage numerous stimulator/response pairs with potential applications (Verma & Khanna, 2022). The above definition covers a wide range of coatings and includes anti-corrosive, self-healing, antibacte-rial, drug delivery, optical, camouflage potential and electrical protection functions (Montañez et al., 2020; Java Verma, Subhasha Nigam, Surbhi Sinha, & Arpita Bhattacharya, 2018). The most important sectors of demand for smart coatings are military, healthcare, energy, aerospace and transportation. Experts believe that the higher cost of smart coatings will continue to be significant for the foreseeable future. Various attempts have been made to reduce costs, including an increase in serviceable life or functionality and the reduction of installation costs (Shi et al., 2009). New smart coatings which do not meet these requirements are unlikely to find commercial applications. It should be noted that smart coatings are closely related to smart surfaces. The terms are sometimes interchangeable because of their more common applications. In military industries, partic-ularly in the USA, there has traditionally been a better market for advanced and specialized smart surfaces.

The two main market areas for smart coatings in military industries are anti-corrosion and camouflage. The annual cost of corrosion to the Department of Defense of the United States is estimated to be above \$20 billion. Some \$4 billion has been spent on coating and painting equipment and structures. To reduce these costs, the Department of Defense has contracted with companies to produce smart surfaces for minimizing corrosion problems and designing fast alarm systems. These coatings transmit signals such as a simple colour change or flaming under fluorescent light during the corrosion process. Likely, future self-repairing coatings will also be able to repair corrosion (Verma, Bennett, & Goel, 2022). There are several advantages to such smart surfaces: reduced staff hours required for maintenance, longer equipment life, an increase in serviceable life under harsh environments and economic savings. Although self-repair surfaces offer a higher average life, the necessity of applying warning systems is also emphasized (T. Khaleque & S. J. M. T. P. Goel, 2022; Viswanathan, Katiyar, Goel, Matthews, & Goel, 2021).

5. CONCLUSION

Coatings provide a sustainable measure to protect bulk surfaces, especially those deployed in harsh environ-ments. Nowadays, materials with a special chemical, physical and physicochemical properties can enhance anti-corrosion and antiwear performance. The effectiveness of nanocomposite coatings generally depends on a variety of unspecified parameters. Additionally, it has been discovered that even a slight change in a small parameter can significantly impact the characteristics and abilities of nanocomposite coatings. Hence, trade and business have not acknowledged the accomplishments of those nanocomposite coatings for potential ap-plications in numerous areas. Finding specific nanocomposite coatings with beneficial, consistent, and repro-ducible protective characteristics takes a lot of effort. The nanomaterials themselves also have issues, such as the lack of control over their size, shape, and features. Fundamental difficulties, including successfully assem-bling nanoparticles in their nanocomposite for practical research, are closely connected to the characteristics of nanocomposite coatings. Homogeneous dispersion, morphology and size control, surface chemistry of small nanomaterials, and ineffective interfacial contact control are the main obstacles to successfully combining those two components into a single element to reinforce the feature. Experts' ability to resolve the issues relating to protective use in many industries, such as domestic, marine, building, and defence, will determine the future of these particular coating markets. This alludes to the need of digitalization in the surface manufacturing sec-tor which is an ongoing effort.

6. FUTURE OPPORTUNITIES

Advances in multifunctional coatings have produced almost perfect metallic materials, regarding their mechan-ical properties, availability and costs, which perform excellently in many structural applications. However, their lack of chemical stability in corrosive environments needs to be addressed, increasing maintenance and overall costs during their lifespan. Epoxy resins and polyurethane-based coatings, acting as artificial barriers to sepa-rate the steel from the corrosive environment, are some of the most commonly employed materials as corrosion protection systems with applicability in a

wide range of marine transports and infrastructures (Verma, Khanna, & Bhattacharya, 2021). These protection systems may contain chemicals like binding agents, pigments, or colorants for, among others, naval traffic security reasons (Valdez et al., 2016). These organic components are susceptible to being released from the coatings upon contact with seawater through leaching or weathering pro-cesses or material losses. For a specific coating product, several factors, such as their concentration/ viscosity, how the coating is applied, the salinity of seawater, exposure to sunlight, stress corrosion cracking processes, etc., determine their released quantity (Kirchgeorg et al., 2018). Thus, developing new forms of protection against corrosion based on eco-friendlier materials with intrinsic durability, good substrate adhesion and ade-quate mechanical properties is key to withstand external stresses, mechanical solicitation, or weathering while minimizing the release of toxic substances during their application and operation times (Faisal *et al.*, 2022; Teijido et al., 2022).

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