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Marine Superhydrophobic Coatings: Core–Shell Materials and Applications

Agni Mohapatra* 

Department of Chemical Engineering, IT Delhi, India

*Corresponding Author: Agni Mohapatra, Department of Chemical Engineering, IT Delhi, India.

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Abstract

Marine infrastructures and vessels continuously face challenges associated with corrosion, biofouling, ice accumulation, drag resistance, and contamination resulting from prolonged exposure to seawater. Superhydrophobic materials have emerged as promising solutions owing to their ability to repel water, reduce surface adhesion, and provide self-cleaning characteristics. However, conventional superhydrophobic coatings often suffer from poor mechanical durability and degradation under harsh marine conditions. Core–shell structured particles offer an advanced approach to overcome these limitations by integrating mechanically robust cores with functional hydrophobic shells. Such architectures enable the development of durable, multifunctional, and environmentally resilient superhydrophobic coatings. This review discusses the fundamental principles governing superhydrophobicity, fabrication strategies for core–shell particles, material selection, coating preparation methods, and their applications in marine operations. Particular emphasis is placed on anti-corrosion, antibiofouling, anti-icing, drag reduction, and oil–water separation technologies. Current challenges and future opportunities for large-scale industrial implementation are also highlighted.

Keywords: Core–Shell Particles, Superhydrophobicity, Marine Coatings, Anti-Corrosion, Biofouling Prevention, Drag Reduction, Oil–Water Separation

Introduction

Marine environments represent some of the most aggressive operational conditions encountered by engineering material [1]. High salinity, humidity, dissolved oxygen, microbial activity, and mechanical abrasion collectively accelerate material degradation [2]. Corrosion alone contributes billions of dollars annually to maintenance and replacement costs in offshore structures, ships, pipelines, and marine equipment [3].

Nature provides inspiration through surfaces such as lotus leaves, water strider legs, and butterfly wings that exhibit remarkable water repellency. These surfaces possess hierarchical micro/nanostructures combined with low surface energy chemistry, resulting in water contact angles exceeding 150° and sliding angles below 10°. Such surfaces are classified as superhydrophobic [4,5].

While numerous superhydrophobic coatings have been developed, their practical application in marine operations remains limited due to insufficient durability. Core–shell particles address this challenge by combining structural robustness and functional versatility. The core provides mechanical strength and adhesion, whereas the shell contributes surface roughness and hydrophobic chemistry [6]. Consequently, core–shell particle-based coatings have become increasingly attractive for next-generation marine protective technologies.

Fundamentals of Superhydrophobicity Wetting Theories

Surface wettability is commonly described using Young's equation:

$$\frac{\gamma_{sv} - \gamma_{SL}}{\cos\theta} =$$

where θ is the contact angle and γ represents interfacial tensions.

Two primary models explain superhydrophobic behavior:

Wenzel Model

Water completely penetrates surface roughness.

$$\cos\theta_w = r\cos\theta$$

where r is the roughness factor.

Cassie–Baxter Model

Air pockets remain trapped beneath water droplets.

$$\cos\theta_c = f(\cos\theta + 1) - 1$$

where f represents the solid fraction in contact with water.

The Cassie–Baxter state is generally preferred for marine applications because trapped air minimizes liquid-solid contact and reduces adhesion.

Core–Shell Particle Architecture

Core–shell particles consist of two distinct regions:

Core Functions:

- Mechanical reinforcement
- Structural stability
- Impact resistance
- Cost reduction
- Thermal stability

Shell Functions:

- Surface roughness generation
- Low surface energy modification
- Corrosion resistance
- Functional responsiveness

The combination creates multifunctional particles capable of maintaining superhydrophobicity under harsh marine conditions.

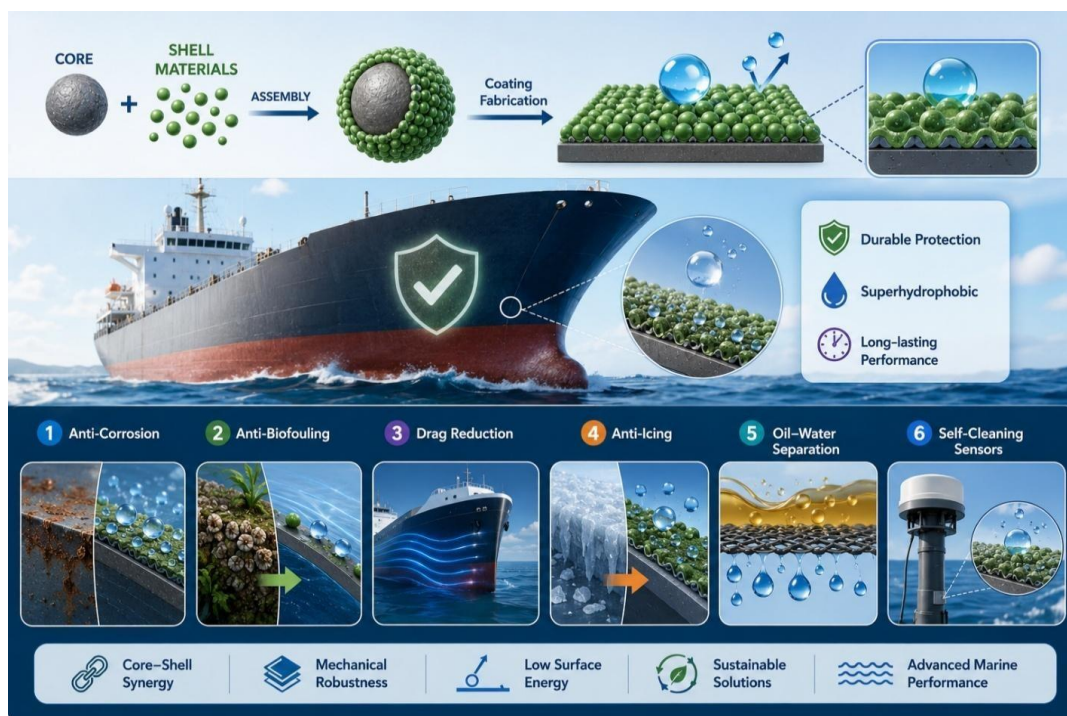


Figure 1: Core Shell Particle Architecture

Materials Used in Core–Shell Superhydrophobic Particles

Silica-Based Systems

Silica-based core–shell particles are among the most extensively studied materials for the fabrication of superhydrophobic surfaces due to their excellent physicochemical properties and ease of synthesis. Silica (SiO_2) particles offer highly tunable morphologies, allowing precise control over particle size, shape, and surface roughness, which are critical

factors in achieving superhydrophobic behavior. Additionally, silica exhibits high chemical and thermal stability, making it suitable for harsh marine environments where coatings are exposed to seawater, UV radiation, and mechanical stresses. The abundance of surface hydroxyl groups on silica particles enables straightforward functionalization with a wide range of hydrophobic agents, facilitating the development of tailored surface chemistries. Furthermore, silica precursors are relatively inexpensive and readily available, supporting large-scale production and industrial applicability. Common examples of silica-based core-shell systems include SiO_2 @PDMS, SiO_2 @fluorosilane, and SiO_2 @PTFE structures, where the silica core provides mechanical robustness and micro/nanoscale roughness, while the outer shell contributes low surface energy characteristics. These combined features generate hierarchical surface architectures capable of trapping air pockets and maintaining a stable Cassie-Baxter wetting state, thereby imparting excellent water repellency, self-cleaning ability, and long-term superhydrophobic performance.

Polymer-Based Systems

Polymer-based core-shell particles have attracted significant attention for the development of superhydrophobic coatings owing to their low density, versatility, and ease of large-scale production. Common polymeric core materials include polystyrene (PS), poly(methyl methacrylate) (PMMA), polyurethane (PU), and epoxy microspheres, each offering distinct advantages in terms of mechanical properties, flexibility, and processability. The lightweight nature of polymer cores makes them particularly suitable for marine coatings, where minimizing additional weight is often desirable. Moreover, polymer particles can be synthesized with controlled sizes and morphologies through scalable techniques such as emulsion polymerization and suspension polymerization, facilitating industrial implementation. In core-shell architectures, the polymer core typically serves as a mechanically supportive framework, while the shell introduces surface roughness and hydrophobic functionality required for superhydrophobic behavior.

Representative examples include PS@SiO_2 , PMMA@fluorosilane , and PU@silica systems, where silica or fluorinated shells create hierarchical micro/nanostructures and reduce surface energy. These coatings exhibit enhanced water repellency, flexibility, and adhesion to substrates, making them promising candidates for anti-corrosion, anti-fouling, and self-cleaning applications in marine environments.

Metal and Metal Oxide Systems

Metal and metal oxide-based core-shell particles have emerged as highly effective materials for superhydrophobic marine coatings due to their superior mechanical strength, chemical stability, and multifunctional properties. Commonly employed materials include titanium dioxide (TiO_2), zinc oxide (ZnO), aluminum oxide (Al_2O_3), and magnetite (Fe_3O_4), which can serve either as core materials or as functional shell layers. These materials offer several advantages over purely polymeric systems, including enhanced hardness, improved wear resistance, excellent thermal stability, and resistance to harsh environmental conditions. Additionally, TiO_2 and ZnO exhibit strong UV resistance, helping to prevent photodegradation of coatings during prolonged outdoor exposure. Fe_3O_4 -based particles provide magnetic responsiveness, enabling controlled manipulation, recovery, or targeted deposition in specialized applications. Furthermore, metal oxide shells can act as physical barriers against moisture and corrosive ions, thereby enhancing corrosion protection in marine environments. Representative examples include Fe_3O_4 @ SiO_2 , TiO_2 @PDMS, and ZnO@fluorosilane core-shell systems, where the combination of robust inorganic materials and low-surface-energy coatings generates durable superhydrophobic surfaces with excellent anti-corrosion and selfcleaning performance.

Hybrid Nanocomposites

Hybrid nanocomposite core-shell particles represent an advanced class of superhydrophobic materials that integrate multiple nanostructured components to achieve enhanced functionality beyond water repellency. These systems commonly combine carbon nanotubes (CNTs), graphene oxide (GO), silica nanoparticles, and functional polymers within a single hierarchical architecture. The incorporation of carbon-based nanomaterials provides exceptional mechanical strength, electrical conductivity, and thermal stability, while silica nanoparticles contribute micro/nanoscale surface roughness essential for maintaining superhydrophobicity. Functional polymers further improve processability, adhesion, flexibility, and environmental resistance. The synergistic interaction among these components results in coatings with superior durability and multifunctional characteristics. In addition to exhibiting excellent water repellency and self-cleaning behavior, hybrid nanocomposites can offer electrical conductivity, electromagnetic shielding, sensing capabilities, anti-corrosion protection, and stimuli-responsive behavior. Such multifunctionality makes these materials particularly attractive for next-generation marine applications, including smart coatings, structural health monitoring systems, anti-fouling surfaces, and integrated sensing platforms for offshore and naval operations.

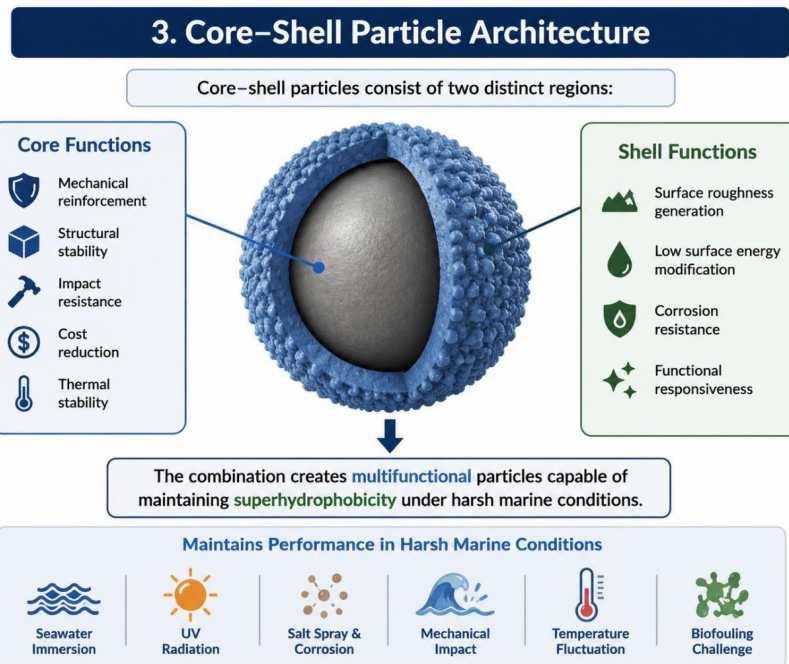


Figure 2: Materials Used in Coreshell Superhydrophobic Particles

Fabrication Strategies

The performance of core–shell superhydrophobic particles is strongly influenced by the fabrication method employed, as it determines particle morphology, shell uniformity, surface roughness, and overall functionality. Among the various synthesis approaches, the sol–gel method remains the most widely used technique due to its simplicity, versatility, and ability to produce highly uniform coatings. This process typically involves the hydrolysis and condensation of metal alkoxide precursors, such as tetraethyl orthosilicate (TEOS), to form a silica shell around polymeric or inorganic cores. The sol–gel route offers several advantages, including low processing temperatures, precise control over shell thickness, excellent shell uniformity, and scalability for large-scale production. Emulsion polymerization is another commonly employed method, particularly for polymer-based core–shell particles. This technique enables the synthesis of highly monodisperse particles with controlled dimensions and shell thicknesses while supporting large-scale manufacturing. For applications requiring precise nanoscale engineering, layer-by-layer (LbL) assembly has emerged as a powerful strategy. In this approach, alternating layers of oppositely charged materials are sequentially deposited onto particle surfaces, allowing exceptional control over shell composition, thickness, and surface functionality. The method is particularly useful for fabricating multifunctional coatings with tailored surface chemistries. Additionally, spray drying and aerosol processing techniques have gained considerable attention for industrial-scale production of core–shell particles. These continuous manufacturing processes are costeffective, scalable, and capable of producing particles with uniform morphology and controlled size distributions. Together, these fabrication strategies provide versatile pathways for designing high-performance core–shell particles suitable for durable superhydrophobic coatings in demanding marine environments.

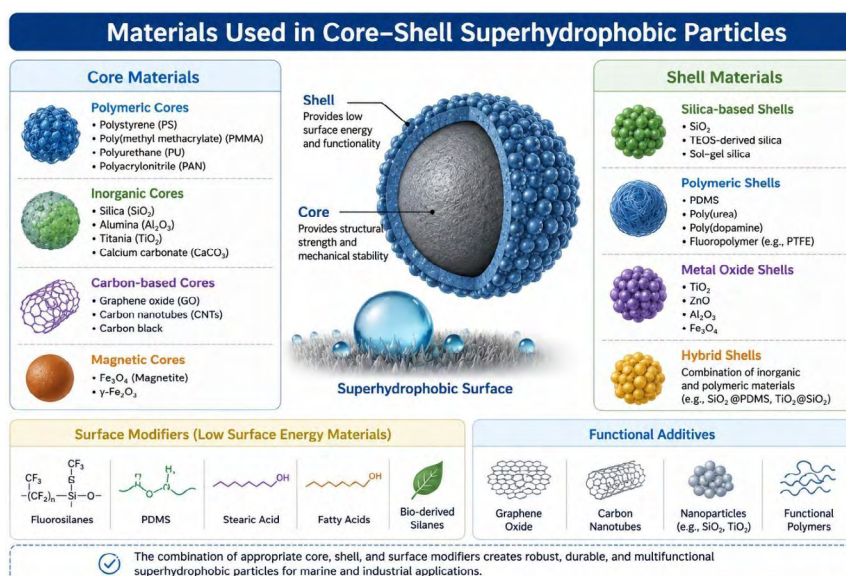


Figure 3: Coating Fabrication Techniques

Coating Fabrication Techniques

The successful implementation of core-shell superhydrophobic particles in marine applications depends not only on particle design but also on the coating deposition technique used to integrate these particles onto substrates. Among the various methods available, spray coating is one of the most widely adopted techniques due to its simplicity, rapid deposition rate, and ability to cover large surface areas efficiently. This method is particularly attractive for marine applications such as ship hulls, offshore platforms, and large structural components where scalable coating processes are required. Dip coating is another commonly used approach, especially in laboratory-scale studies, where substrates are immersed in a particle suspension and subsequently withdrawn at a controlled rate to achieve uniform film formation. The technique is valued for its simplicity and ability to produce consistent coatings on substrates with complex geometries.

Electrophoretic deposition (EPD) has also gained considerable attention because it enables strong particle adhesion and precise control over coating thickness through the application of an electric field, making it suitable for producing durable and uniform protective layers. For research and thin-film applications, spin coating is frequently employed, where a particle suspension is spread across a substrate by centrifugal force to form highly uniform and controlled thin films. Although primarily limited to flat substrates and small-scale fabrication, spin coating remains an important tool for investigating the fundamental properties of superhydrophobic coatings. Collectively, these coating fabrication techniques provide flexible and scalable routes for translating core-shell particle technologies into functional superhydrophobic surfaces tailored for diverse marine environments.

Usefulness in Marine Environments

Anti-Corrosion Coatings

Corrosion remains one of the most critical challenges affecting marine infrastructure, including ship hulls, offshore platforms, pipelines, and underwater equipment. Continuous exposure to seawater, dissolved salts, oxygen, and fluctuating environmental conditions accelerates electrochemical degradation, leading to significant economic losses and maintenance costs. Core-shell superhydrophobic coatings have emerged as an effective strategy for mitigating corrosion by creating a highly water-repellent barrier between the substrate and the surrounding environment. The hierarchical micro/nanostructures generated by core-shell particles trap stable air pockets at the coating surface, significantly reducing the contact area between seawater and the underlying substrate.

Furthermore, the low-surface-energy shell inhibits electrolyte penetration and minimizes the diffusion of aggressive chloride ions responsible for localized corrosion. The synergistic effect of physical barrier protection and trapped insulating air layers suppresses electrochemical reactions, thereby extending coating durability and service life. Numerous studies have reported corrosion current densities that are more than two orders of magnitude lower than those observed for uncoated substrates, demonstrating the remarkable protective capabilities of core-shell superhydrophobic coatings in marine environments.

Anti-Biofouling Surfaces

Biofouling is a persistent problem in marine operations and involves the accumulation of microorganisms, bacteria, algae, barnacles, and other marine organisms on submerged surfaces. The formation of biofouling layers not only increases hydrodynamic drag but also accelerates corrosion and raises maintenance costs. Superhydrophobic surfaces offer an environmentally friendly alternative to conventional biocidal coatings by reducing the likelihood of organism attachment through physical rather than chemical means. The extremely low surface energy and minimized solid-liquid contact area characteristic of superhydrophobic coatings hinder the initial adhesion of fouling species. Additionally, self-cleaning effects facilitate the removal of contaminants through water flow or wave action before permanent attachment can occur. Core-shell particles further enhance the effectiveness of anti-biofouling coatings by improving mechanical robustness and preserving surface roughness under prolonged marine exposure. As a result, these coatings can maintain their anti-fouling performance for extended periods, making them attractive candidates for sustainable marine protection technologies.

Drag Reduction

Hydrodynamic drag is a major factor influencing the fuel consumption and operational efficiency of marine vessels. Even small reductions in drag can translate into substantial energy savings and lower greenhouse gas emissions over the lifetime of a ship. Superhydrophobic coatings based on core-shell particles have demonstrated significant potential for drag reduction by retaining a thin layer of air, known as a plastron, at the solid-liquid interface. This trapped air layer acts as a lubricating barrier that decreases direct contact between flowing water and the vessel surface, thereby reducing liquid-solid friction and flow resistance. The hierarchical roughness generated by core-shell particles promotes the stability of this air layer under dynamic conditions, improving drag reduction performance compared to conventional coatings. Depending on vessel speed, coating durability, and environmental conditions, studies have reported potential fuel savings ranging from 5% to 20%. Consequently, core-shell superhydrophobic coatings represent a promising technology for enhancing marine transportation efficiency while reducing operational costs and environmental impact.

Anti-Icing Applications

Marine vessels operating in polar and subpolar regions frequently encounter ice accumulation on decks, equipment, and structural components. Ice formation can increase weight, compromise stability, hinder equipment functionality, and

pose serious safety risks to personnel and operations. Core-shell particle-based superhydrophobic coatings provide an effective approach to mitigating ice-related issues by minimizing water retention on exposed surfaces. The trapped air pockets and low surface energy associated with these coatings delay ice nucleation and reduce the residence time of water droplets, thereby lowering the likelihood of ice formation. Additionally, the reduced contact area between ice and the coated surface significantly decreases ice adhesion strength, facilitating passive ice removal through wind, vibration, or gravitational forces. These anti-icing characteristics contribute to improved operational safety, reduced maintenance requirements, and enhanced reliability of marine equipment operating in cold-weather environments.

Oil–Water Separation

Oil spills and oily wastewater generated from shipping, offshore drilling, and industrial activities represent significant environmental challenges in marine ecosystems. Efficient separation technologies are therefore essential for pollution control and environmental remediation. Core-shell particle-based superhydrophobic materials have shown exceptional potential in oil–water separation applications due to their unique wetting characteristics. When incorporated into meshes, membranes, or porous substrates, these particles create surfaces that simultaneously exhibit superhydrophobicity and superoleophilicity. Such surfaces strongly repel water while selectively attracting and absorbing oil, enabling efficient gravity-driven separation processes. The hierarchical roughness and tailored surface chemistry provided by core-shell architectures contribute to high separation efficiency, excellent flux rates, and reusability. Many reported systems achieve oil–water separation efficiencies exceeding 98%, highlighting their suitability for marine spill remediation and wastewater treatment applications.

Self-Cleaning Marine Sensors

Marine monitoring systems and sensors play a crucial role in navigation, environmental assessment, structural health monitoring, and offshore operations. However, prolonged exposure to seawater often results in contamination from dirt, salt deposits, microorganisms, and biofouling, which can degrade sensor accuracy and reliability. Superhydrophobic coatings incorporating core-shell particles offer an effective solution by imparting self-cleaning functionality to sensor surfaces. Water droplets rolling across the coating can readily collect and remove contaminants, preventing the accumulation of deposits that interfere with sensor performance. The reduced adhesion of pollutants and marine organisms further minimizes fouling-related issues and extends sensor operational lifetime. Moreover, the enhanced durability provided by core-shell architectures ensures long-term maintenance of superhydrophobic properties under harsh marine conditions. Consequently, these coatings reduce maintenance frequency, improve measurement accuracy, and enhance the overall reliability of marine sensing technologies.

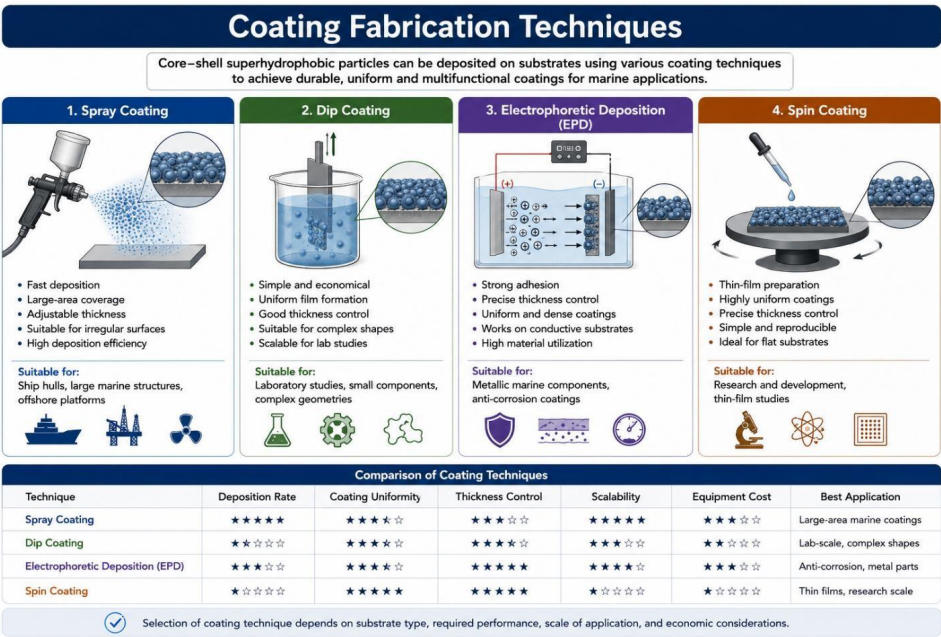


Figure 4: Applications of Coreshell Superhydrophobic Materials in Marine Infrastrutures

Mechanical Durability of Core–Shell Systems

Mechanical durability is one of the most critical requirements for the successful deployment of superhydrophobic coatings in marine environments. While many laboratory-developed superhydrophobic surfaces exhibit excellent water repellency, their practical application is often limited by poor resistance to mechanical and environmental stresses. Marine coatings are continuously exposed to harsh conditions, including abrasion from suspended particles and cleaning operations, impact damage from debris and wave action, prolonged ultraviolet (UV) radiation, salt-induced chemical attack, and repeated mechanical loading that can lead to fatigue-induced degradation. These factors can damage surface micro/ nanostructures and compromise the low-surface-energy layer responsible for superhydrophobic behavior.

Core-shell architectures provide an effective solution to these durability challenges by separating structural and functional responsibilities between the core and shell components.

The core serves as a mechanically robust framework that absorbs and dissipates applied stresses, thereby maintaining the structural integrity of the particle and coating system under demanding conditions. Meanwhile, the shell provides the required surface roughness and low-surface-energy chemistry that impart superhydrophobic characteristics while simultaneously protecting the core from environmental degradation. This synergistic design enhances both mechanical resilience and long-term functionality. Recent studies have demonstrated that core-shell superhydrophobic coatings can retain high water contact angles and low sliding angles even after severe durability tests, including repeated sandpaper abrasion, high-pressure water jet impact, prolonged salt spray exposure, and cyclic immersion in seawater. These findings highlight the superior robustness of core-shell systems and their potential for long-term use in marine applications where durability and sustained performance are essential.

Environmental and Sustainability Considerations

Environmental sustainability has become an increasingly important consideration in the development of superhydrophobic materials for marine applications. Traditionally, many high-performance superhydrophobic coatings have relied on fluorinated compounds due to their exceptionally low surface energy and outstanding water-repellent properties. However, growing concerns regarding the persistence, bioaccumulation, and potential toxicity of fluorinated substances have prompted stricter environmental regulations and increased interest in more sustainable alternatives. In response, researchers are actively exploring environmentally benign hydrophobic materials that can deliver comparable performance without adverse ecological impacts. Promising fluorine-free alternatives include polydimethylsiloxane (PDMS), stearic acid, naturally derived fatty acids, bio-based silanes, and renewable polymeric materials. These compounds offer low surface energy while exhibiting improved biodegradability, lower toxicity, and reduced environmental persistence. Additionally, the integration of such sustainable materials into core-shell architectures can help maintain the hierarchical surface roughness and durability required for long-term superhydrophobic performance. As environmental regulations continue to evolve and demand for green technologies increases, future marine coatings are expected to focus on fluorine-free formulations that combine excellent water repellency, mechanical robustness, and environmental compatibility, thereby supporting the development of sustainable and ecofriendly marine protection systems.

Current Challenges

Despite significant advancements in the development of core-shell superhydrophobic particles for marine applications, several technical, economic, and regulatory challenges continue to hinder their widespread commercial adoption. From a technical perspective, maintaining long-term stability under harsh marine conditions remains a major concern. Prolonged exposure to seawater, mechanical wear, ultraviolet radiation, and biofouling can gradually degrade surface structures and reduce superhydrophobic performance. Additionally, retaining the trapped air layer, which is essential for drag reduction and anti-corrosion functionality, becomes increasingly difficult during extended underwater operation or under high-pressure conditions. Achieving strong and durable adhesion between the coating and substrate is another critical challenge, particularly for large marine structures subjected to continuous mechanical and environmental stresses. Furthermore, translating laboratory-scale synthesis methods into reliable and cost-effective large-scale manufacturing processes remains an ongoing challenge.

Economic considerations also play a significant role in limiting industrial implementation. Many advanced core-shell systems require specialized materials, multiple processing steps, and sophisticated fabrication techniques, resulting in high production costs. The complexity of synthesis routes can further hinder scalability and reduce manufacturing efficiency, making commercial deployment less attractive compared to conventional protective coatings. In addition, regulatory and environmental concerns must be addressed before widespread adoption can occur. Increasingly stringent environmental regulations require comprehensive toxicity assessments of coating materials and their degradation products to ensure minimal ecological impact. The compatibility of these coatings with marine ecosystems is particularly important, as any released particles or chemicals could potentially affect aquatic organisms and biodiversity. Consequently, future research efforts must focus not only on improving coating performance and durability but also on developing economically viable, environmentally responsible, and regulatory-compliant technologies suitable for long-term marine applications.

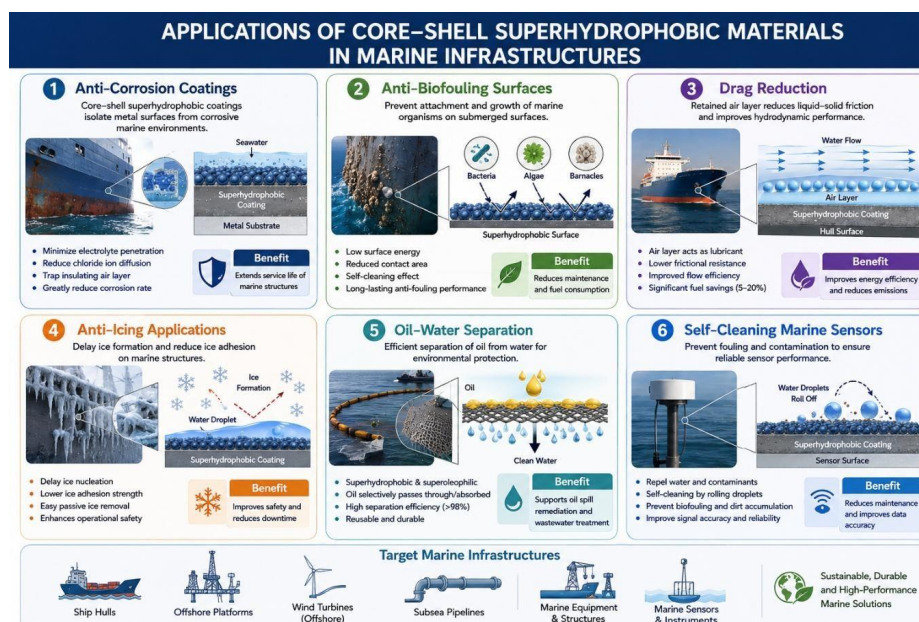


Figure 5: Current Challenges and Future Perspectives on Superhydrophobicity in Marine Applications

Future Perspectives

The future development of core-shell superhydrophobic particles for marine applications is expected to focus on the creation of intelligent, multifunctional, and sustainable coating systems capable of addressing multiple operational challenges simultaneously. One promising research direction involves the development of smart core-shell systems that can actively respond to environmental stimuli and recover from damage. Self-healing coatings, for example, have the potential to autonomously repair microcracks and surface defects generated during service, thereby extending coating lifetime and maintaining superhydrophobic performance. Similarly, stimuli-responsive surfaces capable of reacting to changes in temperature, pH, salinity, light, or mechanical stress could provide adaptive wettability and enhanced functionality under varying marine conditions. Such advanced systems may significantly improve the reliability and durability of marine coatings in dynamic environments.

Another important trend is the design of multifunctional marine coatings that integrate several protective and operational functions within a single platform. Rather than addressing individual challenges separately, future coatings are expected to simultaneously provide anti-corrosion protection, anti-biofouling performance, drag reduction, and sensing capabilities. The unique versatility of core-shell architectures makes them particularly suitable for incorporating multiple functionalities through careful selection of core and shell materials. This multifunctional approach could reduce maintenance requirements, lower operational costs, and improve the overall efficiency of marine structures and vessels.

Advances in additive manufacturing technologies are also expected to play a significant role in the next generation of marine coatings. Techniques such as 3D printing, direct ink writing, and advanced deposition methods offer unprecedented control over material architecture and surface morphology. These technologies may enable the fabrication of customized coatings with precisely engineered micro- and nanostructures tailored to specific marine applications. Furthermore, the integration of artificial intelligence (AI) and machine learning into materials development is emerging as a powerful tool for accelerating innovation. By analyzing large datasets and identifying complex relationships between material composition, particle morphology, and coating performance, AI-driven approaches can significantly reduce the time and cost associated with material optimization. Machine learning algorithms may facilitate the rational design of core-shell particles, optimize shell compositions and fabrication parameters, and predict long-term coating performance, ultimately accelerating the commercialization of advanced superhydrophobic coatings for marine operations.

Conclusion

Core-shell superhydrophobic particles represent a highly promising class of materials for next-generation marine operations. Their unique architecture enables simultaneous enhancement of mechanical durability, corrosion resistance, anti-biofouling behavior, drag reduction, anti-icing performance, and oil-water separation efficiency. By integrating robust cores with functional hydrophobic shells, these materials overcome many limitations associated with conventional superhydrophobic coatings. Although challenges related to scalability, long-term durability, and environmental sustainability remain, rapid advances in particle engineering, surface chemistry, and coating technologies are driving the transition from laboratory demonstrations toward real-world marine applications. Future developments focusing on fluorine-free formulations, self-healing systems, and multifunctional smart coatings are expected to further expand the industrial adoption of core-shell superhydrophobic particles in marine environments.

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