



# Recent Advancements in Graphene Derivative-Based Nanocomposites: Innovations in Coating and Sensing Technologies

Nadia Khan<sup>1</sup>, Zahra A. Tabsi<sup>2</sup>, Baiyu Zhang<sup>3</sup> and Yuming Zhao<sup>2\*</sup>

<sup>1</sup>Faculty of Science, Memorial University of Newfoundland, St. John's, NL, A1B 3X5, Canada

<sup>2</sup>Department of Chemistry, Memorial University of Newfoundland, St. John's, NL, A1C 5S7, Canada

<sup>3</sup>Northern Region Persistent Organic Pollutant Control (NRPOP) Laboratory, Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, NL, A1B 3X5, Canada

**Abstract:** Graphene derivative-based nanocomposites have emerged as innovative solutions to address challenges in corrosion, marine biofouling, and environmental contamination. This review highlights recent advancements in three key areas: (1) dual-barrier and self-healing anti-corrosion materials, (2) eco-friendly anti-biofouling coatings, and (3) high-efficiency electrocatalytic films for electrochemical sensing. We emphasize the critical roles of graphene (Gr) sheets, graphene oxide (GO), and reduced graphene oxide (rGO) in enhancing nanocomposite performance through novel modifications with inorganic materials, organic polymers, and biomolecules. Key insights into advanced modification techniques and their impact on functionality and durability are presented. The review also explores graphene-enabled electrochemical sensors that showed high sensitivity to phenolic compounds in water. Mechanisms accounting for the improved performance of these materials are discussed, along with associated challenges such as scalability, cost-effectiveness, and stability. Future directions are suggested, focusing on sustainable, intelligent coatings and thin-film devices for environmental applications. This work aims to guide researchers, industry professionals, and policymakers in leveraging graphene-based technologies to tackle global issues in corrosion prevention, marine ecology, and environmental monitoring.

Received on 05-10-2024  
 Accepted on 21-11-2024  
 Published on 11-12-2024

**Keywords:** Nanocomposite, graphene derivative, anti-corrosion, anti-biofouling, self-healing, electrochemical sensor, phenolic compounds, metal-organic framework (MOF), biomolecules, graphene oxide (GO), reduced graphene oxide (rGO).

<https://doi.org/10.6000/2369-3355.2024.11.02>

## 1. INTRODUCTION

In recent years, the application of coating materials incorporating graphene and its derivatives as nanoscale functional additives has witnessed significant growth across various industries. These advanced coatings leverage the unique properties of graphene, including its exceptional mechanical strength, electrical and thermal conductivity, and impermeability to gases and liquids. For example, the automotive, aerospace, electronics, marine, medical, and construction sectors have all benefited from graphene-enhanced coatings, which offer superior corrosion resistance,

improved durability, and multifunctional capabilities [1]. It has been known that graphene-infused coatings create tortuous pathways that impede the penetration of corrosive agents, making them particularly valuable in marine corrosion protection [2]. The enhanced mechanical properties of these coatings, such as improved toughness and scratch resistance, are crucial in industries where wear resistance is paramount.

Furthermore, the development of conductive paints and coatings with enhanced thermal management properties has been facilitated by graphene's excellent thermal conductivity [3]. The research community has also been actively exploring multifunctional coatings that combine corrosion resistance, UV protection, flame retardancy, and antimicrobial effects [4]. The environmental benefits of some graphene-based coatings, which reduce the need for harmful chemicals, align

\*Address correspondence to this author at the Department of Chemistry, Memorial University of Newfoundland, St. John's, NL, A1C 5S7, Canada; E-mail: yuming@mun.ca

with growing sustainability concerns. Market projections indicate rapid growth in the global graphene coating sector, with estimates suggesting that it will reach \$998 million by 2032, growing at a CAGR of 23.39% from 2022 to 2032 (<https://www.marketsandmarkets.com/>). Ongoing research and development efforts continue to expand the applications and improve the performance of graphene-based coatings, representing a significant advancement in materials science with far-reaching implications across multiple sectors globally.

Graphene-based nanocomposites have emerged as revolutionary materials in modern nano-science and technology, offering new materials with exceptional mechanical strength, electrical conductivity, thermal stability, and high surface area [5]. In recent years, the development of graphene-based nanocomposites has led to transformative applications in coating technologies and relevant fields. Nanocomposites are heterogeneous materials composed of two or more different nanoscale components. They can gain unique qualities and properties when graphene and its derivatives are applied as constituents. Graphene and its derivatives have found wide application in coating technologies owing to their inherent properties, providing technical solutions for high-performance coatings with enhanced protective functions and durability. Recent studies have demonstrated the benefit of using graphene and graphene oxide to gain improved corrosion resistance for coatings due to their barrier and lubrication effects [6]. On the other hand, antifouling effects can arise from the non-leaching and environmentally friendly characteristics of graphene-based materials [7, 3].

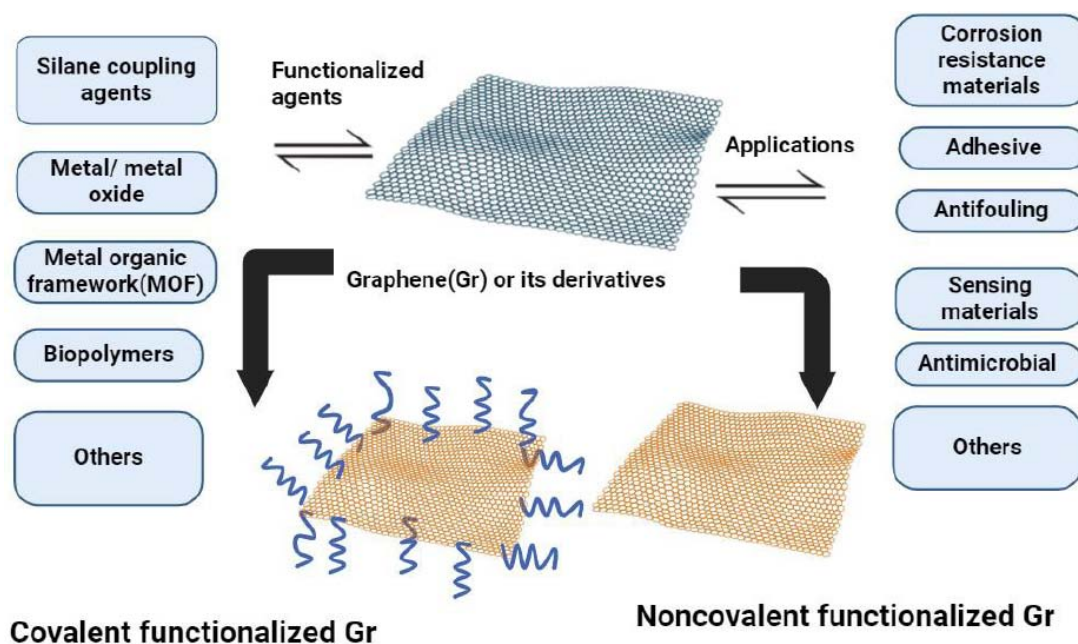
While graphene-based nanocomposites have demonstrated remarkable potential in advancing coating technologies, their application extends beyond protective layers to functional thin-film optoelectronic devices [8,9]. One remarkable subject of research is the emergence of graphene-enabled thin film sensor devices, especially electrochemical sensors for organic pollutants in the environment [10]. Graphene and its derivatives (e.g., graphene oxide and reduced graphene oxide) are electrochemically active materials that show high responsiveness to various chemical species at the interface [11]. These properties are attributable to the exceptional electrical conductivity, high surface area, and flexible tunability of graphene [12]. Extensive studies have demonstrated the remarkable effectiveness of graphene-based chemical sensors in detecting various environmentally important analytes, ranging from metal ions [13], toxic gas molecules [14], and emerging organic pollutants [15-17]. The advantages of graphene-based electrochemical sensors lie in enhanced sensitivity, improved selectivity, wide detection ranges, fast response times, and good stability. Recent progress in this area has showcased the efficacy of graphene-modified electrodes in detecting harmful phenolic compounds such as *p*-nitrophenol [18], catechol [19], resorcinol [20], and 2,4-dinitrobenzene [21] in environmental water samples with excellent sensitivity and selectivity. The

development of these sensors involves strategies such as direct use of graphene or its derivatives, incorporation into composite materials, and functionalization with specific molecules or nanoparticles to enhance selectivity [9]. Ongoing research activities mainly focus on optimizing synthetic methods, exploring novel graphene derivatives, and developing new composite materials to create sensors that are not only highly sensitive and selective but also cost-effective and suitable for large-scale production and application. The use of graphene-derived nanocomposites in electrochemical sensing has played a significant role in advancing the technologies of environmental monitoring and regulation. Compared with traditional analytic methods, the deployment of graphene-based thin film sensors has special advantages in terms of rapid, on-site detection of various pollutants crucial for environmental protection and public health. As research progresses, it is anticipated that the development of more sophisticated and efficient graphene-based chemical sensors will eventually move the technology into real-world applications, revolutionizing the field of environmental sensing and monitoring [22].

Unlike many existing reviews that broadly cover graphene-based technologies [16,23], this review article casts light on the diversity of graphene-enabled interfacial functions, spanning from passive protection to active electron transfer for sensing applications. This distinctive approach to literature survey bridges the gap between seemingly disparate applications of various graphene derivatives, offering a unified perspective in future research on how graphene derivatives continue to excel across various interfacial roles. We believe that the diverse research of graphene derivative-based nanocomposites over the past few years has created a pressing need for a special review article focusing on their applications in anti-corrosion, antifouling, and electrochemical sensing of environmental pollutants. We anticipate the following review to serve as a crucial resource that facilitates and inspires future research in functional interfacial materials, where graphene and graphene derivatives are utilized as key functional ingredients.

## **2. GRAPHENE AND ITS IMPORTANT DERIVATIVES**

Graphene is a carbon material composed of a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice [24]. The history of graphene, from its conceptual origins to its groundbreaking isolation, spans over a century of scientific inquiry and discovery. The journey began in 1859 when Benjamin Collins Brodie unknowingly observed graphene oxide while studying thermally reduced graphite oxide. In 1947, P. R. Wallace laid the theoretical groundwork by exploring graphene's electronic properties as a model for 3D graphite [25]. The term "graphene" was coined in 1986 by Hanns-Peter Boehm, Ralph Setton, and Eberhard Stumpp, combining "graphite" with the suffix "-ene." However, the landmark breakthrough came in 2004 when Andre Geim and Konstantin Novoselov at the University of Manchester



**Figure 1:** Structure of graphene (Gr) and important graphene derivatives.

successfully isolated and identified single-layer graphene using a simple mechanical exfoliation method, famously known as the "scotch tape method". Their groundbreaking results include graphene fabrication, identification, and characterization [26]. The publication of their discovery in 2005 soon sparked a new wave of research in next-generation carbon nanomaterials, revolutionizing composite materials science and application. The pioneering work by Geim and Novoselov was recognized with the Nobel Prize in Physics in 2010, awarded to them "for groundbreaking experiments regarding the two-dimensional material graphene." The isolation of graphene in 2004 and the subsequent Nobel Prize in 2010 catalyzed an explosion of research interest, exploring its unique properties and potential applications in fields ranging from electronics to energy storage and biomedical technologies, marking a new era in materials science and nanotechnology [27,28].

The exceptional flexibility and ease of functionalizing graphene to generate various derivatives have positioned it as a highly functional material for diverse applications [29]. However, pristine graphene itself presents challenges in material integration due to its strong tendency to aggregate and poor compatibility with other substances. This limitation has led researchers to focus on graphene derivatives, which offer more flexible and wider applicability in composite materials. Graphene's large surface area and planar  $sp^2$ -hybridized carbon atoms allow for chemical modifications through both covalent and non-covalent methods, enabling the attachment of various functional groups for tailoring properties such as solubility, reactivity, and electronic characteristics. Graphene oxide (GO) and reduced graphene oxide (rGO) are two prominent derivatives of graphene that exemplify the advantages of using functionalized graphenes.

These derivatives contain reactive functional groups that facilitate covalent and non-covalent interactions with a diverse range of substances, including inorganic compounds, organic molecules, bio-polymers, and macromolecules. Compared with graphene, GO exhibits improved water solubility, abundant oxygen-containing functional groups, enhanced bio-compatibility, and tunable electronic properties.

Nevertheless, the high degree of oxidation in GO introduces many saturated  $sp^3$  carbon centers and other defects in the graphene structure, causing a substantial loss of electric conductivity and mechanical strength. In the area where excellent electronic properties are desired, GO shows limited application. rGO provides a balance between restored electrical conductivity and retained functional groups for further modifications. rGO is prepared by reduction of GO through various approaches. Therefore, rGO structurally contains graphene-like nanosheets and much less defects. This versatility allows for the creation of composite materials with a large array of counterparts, significantly expanding the potential applications of rGO-based materials. Other derivatives, such as graphene quantum dots and nanoribbons, have also emerged to offer unique optical and electronic properties for specialized applications [13]. However, this review does not include their application in coating and electrochemical sensing.

GO is typically prepared through graphite oxidation, most commonly using variations of Hummers' method, which involves the use of potassium permanganate, sodium nitrate, and sulfuric acid as reagents. Recent improvements, such as the Tour method, have led to more efficient and environmentally friendly processes, resulting in higher yields and more regular structures [30]. The reaction mechanism for the formation of GO involves oxidation of graphite, exfoliation

to produce GO sheets and subsequent purification. Structurally, GO contains various oxygenous functional groups, ranging from epoxy and hydroxyl to carboxyl groups. It is therefore not surprising to see GO possesses hydrophilicity and dispersibility in water, which sharply contrasts the hydrophobic nature of graphene. These properties are particularly advantageous for applications in aqueous environments or for further functionalization through solution phase reactions. rGO is produced by reducing GO to partially restore the  $sp^2$  carbon network. Its synthesis can be achieved by chemical reduction of GO using agents like hydrazine, sodium borohydride, or ascorbic acid.

In addition, thermal reduction, electrochemical reduction, photocatalytic reduction, and microwave-assisted reduction have also been developed to generate rGO from GO. Among numerous reduction approaches, chemical reduction is the most common, often performed at room temperature or under mild heating [31]. As such, the chemical reduction of GO is particularly suitable for large-scale production of rGO [32]. Thermal reduction is typically conducted at temperatures above 200°C and requires an inert or reducing environment. Under these conditions, the oxygenous groups in GO can be effectively removed. However, thermal treatment still leads to structural defects in the resulting rGO. Electrochemical reduction offers reasonable control over the degree of reduction and can be performed under mild conditions [33]. Photocatalytic reduction, using UV light or sunlight with photocatalysts, is environmentally friendly but somewhat slower and less efficient than other techniques [34]. Microwave-assisted reduction provides a rapid method for GO reduction [35]. Overall, the choice of reduction method significantly affects the properties of the resulting rGO, determining its electrical conductivity, surface area, and remaining functional groups.

Both GO and rGO offer unique advantages in materials applications. GO's hydrophilicity and abundance of functional groups make it useful in water purification and drug delivery and a versatile precursor for further functionalization. The conversion of GO into rGO improves electrical properties and facilitates applications in conductive coatings, sensors, and energy storage devices. In recent years, research on the production and functionalization methods for GO and rGO continue to grow, leading to more efficient, scalable, and environmentally friendly synthetic methods; for example, "green" reduction methods, such as using plant extracts or environmentally benign reducing agents, and development of hybrid materials that combine GO or rGO with other nanomaterials to create multifunctional composites [36]. Furthermore, researchers are investigating the use of GO and rGO in emerging fields such as flexible electronics, wearable devices, and advanced energy storage systems [37,91,92]. These materials greatly expand the scope of graphene-based technologies and foster more innovations in materials science and nanotechnology [38].

### 3. GRAPHENE DERIVATIVE-BASED NANOCOMPOSITES

Graphene and its derivatives have been popularly applied as additives for polymer matrices, offering a wide range of benefits in the development of nanocomposite polymers. The integration of graphene components into polymers results in hybrid materials with significantly altered properties, including improved electrical conductivity, mechanical strength, and adsorptive capabilities. The large surface area of graphene provides numerous active sites for physical and chemical interactions, enhancing the catalytic and sensing performance of these composites. Notably, graphene's efficient electron transfer properties and electrocatalytic behavior accelerate electrochemical reactions, making these materials valuable for applications in energy storage, flexible electronics, and chemical sensing. The high mechanical strength of graphene contributes to reinforcing the durability of nanocomposites, resulting in materials with improved tensile strength, modulus, and fracture toughness. Furthermore, graphene's ballistic heterogeneous electron transfer property ensures faster and more efficient electron transfer processes, which are crucial for applications in high-performance electronics and energy storage devices [39,40].

Recent research has been focused on optimizing the dispersion of graphene in polymer matrices, often utilizing functionalized forms such as GO and rGO to address the technical challenges of poor dispersion and agglomeration associated with pristine graphene. The development of multifunctional nanocomposites that combine enhanced mechanical properties with electrical conductivity and thermal stability has opened new possibilities in aerospace and automotive applications [41]. In the field of energy storage, graphene-polymer nanocomposites are being investigated for their potential to improve the performance of supercapacitors and lithium-ion batteries [42]. Additionally, the strong adsorption capability of graphene-based composites has found applications in gas separation, water purification, and pollutant removal [43]. Researchers have also explored various fabrication methods, including solution mixing, melt blending, in-situ polymerization, and layer-by-layer assembly, to optimize the integration of graphene into polymer matrices [44]. Challenges remain in achieving uniform dispersion, optimizing interfacial interactions, and developing cost-effective production methods for large-scale applications. Ongoing research efforts are directed toward innovative synthetic techniques, surface modifications of graphene, and new processing methods to overcome these limitations. Recent trends include the development of "green" synthetic methods for graphene derivatives, exploring synergistic effects with other nanomaterials, and creating hierarchical and multifunctional nanocomposites [45]. Emerging areas of interest include self-healing nanocomposites using graphene derivatives [46], stimuli-responsive smart materials [47], and biodegradable graphene-based nanocomposites [48]. As the field progresses, graphene-based polymer nanocomposites are expected to find increasingly diverse applications across

various scientific disciplines and industrial sectors, for instance, nanoelectronics, sustainable energy, environmental remediation, and biomedical engineering, just to name a few [49-51]. The integration of artificial intelligence (AI) in material design and optimization is also expected to accelerate the development of novel graphene-based nanocomposites with tailored properties. These advancements will likely lead to revolutionary advancements in modern materials science and technology [52].

Apart from molecular and macromolecular materials, graphene derivatives can be generated by functionalization of graphene with metal/metal oxide nanoparticles, metal-organic frameworks (MOFs) [53], and covalent organic frameworks (COFs) [54]. The intermarriage of graphene with advanced nanomaterials opens new avenues for developing high-performance functional materials for various applications. For example, graphene-nanoparticle hybrids have shown remarkable improvements in catalytic activity, sensing capabilities, and energy storage performance. Incorporating metal nanoparticles (e.g., Au, Pt, Pd) onto graphene sheets has enhanced electrocatalytic properties for fuel cells and water-splitting applications. Similarly, combining graphene with semiconductor nanoparticles (e.g., TiO<sub>2</sub>, ZnO) has improved photocatalytic activity and solar energy conversion efficiency [55,56]. In the realm of highly porous materials, graphene-MOF composites have demonstrated superior gas adsorption, separation, and storage properties compared to their individual components [57]. The high surface area and electrical conductivity of graphene, combined with the tunable porosity and functionality of MOFs, have led to novel hybrid materials with enhanced CO<sub>2</sub> capture, hydrogen storage, and catalytic efficiency.

Furthermore, the integration of graphene with MOFs has resulted in materials with improved stability, conductivity, and surface area, finding applications in energy storage devices, gas separation membranes, and heterogeneous catalysis [58]. Many of these graphene-based hybrid nanocomposites exhibit synergistic effects of their constituents, while their combination leads to properties and performances that surpass those of the individual components. Ongoing research in this field focuses on optimizing synthetic methods, understanding interfacial interactions, and exploring new combinations of graphene derivatives with advanced nanomaterials to further expand their potential applications in environmental remediation, biomedical engineering, and advanced energy technologies [59,60].

#### 4. RECENT PROGRESSES IN GRAPHENE DERIVATIVE-BASED NANOCOMPOSITES FOR COATING APPLICATION

##### 4.1. Self-Healing and Passive Barrier Coatings

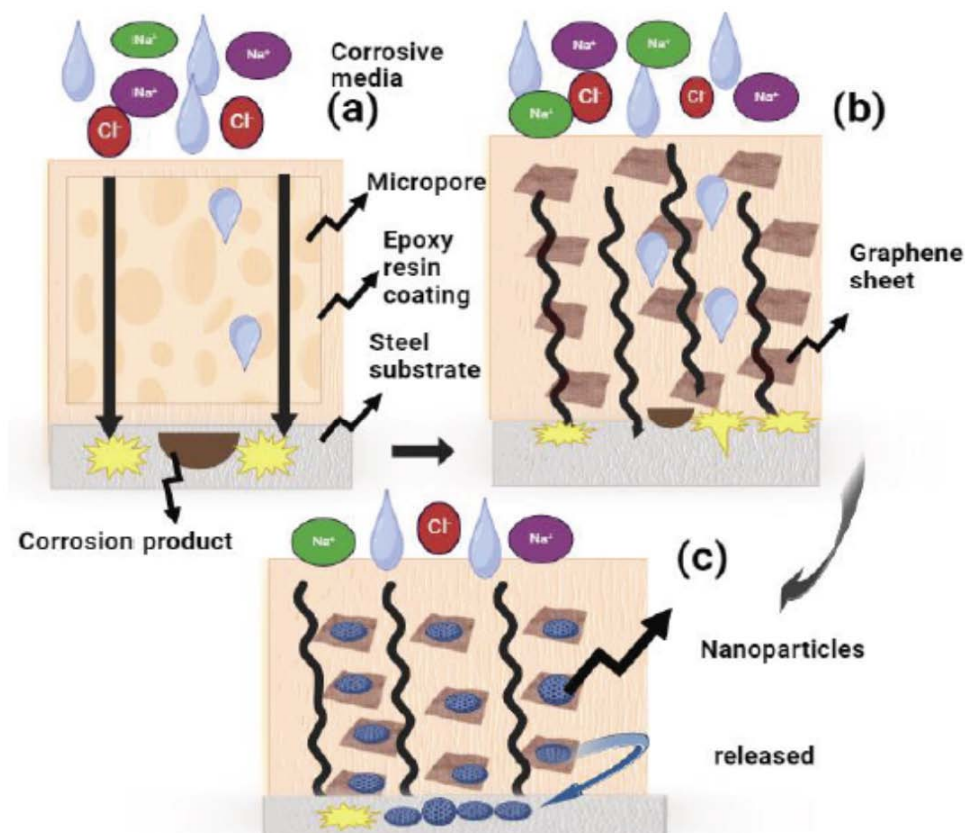
Self-healing anti-corrosion coatings have garnered significant attention, and their continued development is expected to profoundly impact corrosion protection technologies. Usually,

self-healing anti-corrosion coatings work through several mechanisms, such as microcapsules [61,62], reversible chemical bonds [63], or shape memory polymers to autonomously repair damage and maintain continuous protection [64]. In this area, graphene derivative-based nanocomposites have emerged as excellent candidate materials due to their exceptional barrier properties, high surface area, and chemical stability.

Ye *et al.* in 2020 conducted a study in which graphene sheets were prepared to contain porous polyhedral oligomeric silsesquioxane (POSS) nanocontainers through a chemical grafting reaction [65]. These nanocontainers, derived from 8-POSS, paraformaldehyde, and GO, were incorporated into a self-healing organic coating. To create a self-healing organic coating nanocomposite, a corrosion inhibitor benzotriazole (BTA) was loaded into the porous graphene sheets, which were then embedded into an epoxy (EP) coating. The results demonstrated that the graphene-based nanocomposite coating exhibited effective corrosion resistance and highly efficient self-healing properties. The improved coating performance was attributed to the enhanced compactness and the controlled release of BTA. Their study also evaluated the anti-corrosion protective effects in two aspects. First, the formation of an adsorption layer on the metal surface occurred through the release of BTA from the nanocontainer. Second, the graphene sheet acted as a physical barrier, preventing the permeation of the corrosion medium. Barrier properties were further investigated by immersing the 8-PG-BTA/EP composite coating in a 3.5 wt% NaCl solution for 90 days. The results showed that the water absorption of the 8-PG-BTA/EP coating was only 2.87%, which is significantly lower than that of the EP (3.89%) and 8-PG/EP (6.51%). Based on the experimental findings, it was concluded that 8-PG-BTA/EP exhibited the best barrier properties and was considered an optimal anti-corrosion coating, capable of restoring its protective properties after damage from the surrounding environment. In Figure 2, the physical barrier effect of graphene nanocomposite is schematically illustrated, where graphene sheets create a tortuous path for the diffusion of molecules and ions (corrosive species) in the polymer matrices. This significantly enhances the material's ability to act as a barrier against corrosive species, improving resistance to permeability and enhancing the durability and performance of the base material. These barrier effects are particularly beneficial in applications such as protective coatings, packaging, and membranes, where preventing the passage of moisture, oxygen, and other contaminants is crucial. Additionally, the mechanical strength and flexibility of GO further contribute to the integrity and longevity of the composite material, offering a promising solution for advanced barrier technologies.

Mechanistically, graphene-based nanocomposite shows anti-corrosion effects in three key stages of the corrosion process. First, corrosion initiation through water absorption on the coating surface is controlled by transforming the coating





**Figure 2:** Schematic illustration of organic coating layers (a) without any further physical barrier effect, (b) with the physical barrier effect delivered by graphene sheets, and (c) with the physical barrier effect delivered by GO-based nanocomposites.

surface from hydrophilic to hydrophobic. The superhydrophobic nature of the coating promotes self-cleaning by repelling water and, along with it, any attached marine organisms. This self-cleaning effect helps maintain the coating's effectiveness over time. Second, micro-cracks, defects, and cavities in the coating matrix, facilitating electrolyte solution diffusion, can be minimized by modifying GO derivatives with inorganic (e.g., CuO, TiO<sub>2</sub>, SiO<sub>2</sub>), organic (e.g., polymers), and bio-inspired materials (chitosan and dopamine). Modifying the GO surface facilitates homogeneous dispersion in the polymer matrix, which improves the coating's resistance to corrosive agent diffusion. Generally speaking, graphene derivatives such as GO and rGO can form a physical barrier within the nanocomposite coating. This barrier serves as a protective layer that blocks the diffusion path of corrosive agents, such as moisture and aggressive ions, slowing down the rate at which the corrosive species reach the underlying substrate. Due to the hydrophilic nature of GO resulting from numerous oxygen-containing groups (e.g., COOH, OH, epoxy) abundantly existing on the GO structure, GO sheets can readily form agglomeration in the coating matrix. This phenomenon creates more pathways for electrolyte diffusion in the coating matrix.

Moreover, functionalized GO (f-GO) can be efficiently dispersed in the polymer matrix through covalent bonding

between the specially tailored functional groups in GO and the reactive units in polymer backbones. This type of chemistry can be effectively induced during the curing process, leading to enhanced cross-linking density of the polymer coating and improved interfacial bonding between f-GO and the polymer matrix. Through this strategy, f-GO nanocomposites can be designed to achieve excellent barrier effects against the diffusion of corrosive agents into the polymer matrix. Another mechanism for enhanced barrier effects is the incorporation of f-GO into a polymer matrix, which can reduce coating degradation and coating delamination. This effect not only hinders the penetration of corrosive agents through the polymer matrix but strengthens the bonding between the coating layer and the metallic substrate by forming hydrogen bonding with the hydrated oxide film on the steel substrate. As a result, the interfacial adhesion of the coating is increased, and so is its corrosion protection performance. Third, graphene derivatives may inherently inhibit corrosion by adsorbing on the metal surface, hindering electrochemical reactions of corrosion owing to the electronic properties of graphene. This adsorption effect passivates the metal surface, reducing its susceptibility to corrosion.

The anti-corrosion performance of GO coatings can be further enhanced by incorporating self-healing mechanisms. For example, f-GO can be designed to act as nanocarriers

with corrosion inhibitors encapsulated. Adding this function to the coating allows it to autonomously repair damages caused by scratches, cracks, and corrosion. The self-healing function can be activated by various environmental stimuli, such as changes in pH, temperature, or the presence of specific ions. These stimuli trigger the release of the self-healing agents trapped in the nanocontainers in the polymer matrix. The released healing agents then react with the corroded areas to form a protective barrier, repairing the damage and preventing the attack of the metal surface by corrosive agents. Graphene derivative-based nanocomposites are employed to enhance corrosion protection by improving both the preventive measures against corrosive agents and the automatic repair processes when damage occurs (Figure 3).

Nanocomposite coatings can also be designed to exhibit anti-biofouling properties. The graphene sheets contribute to the creation of a superhydrophobic surface with low surface energy and high roughness, as well as the growth of a micro- and nanoscale hierarchical structure. This surface characteristic deters the adhesion of marine organisms and hence inhibits biofouling. There are several factors that influence the self-healing anti-corrosion and anti-biofouling activity of graphene derivative-based nanocomposite

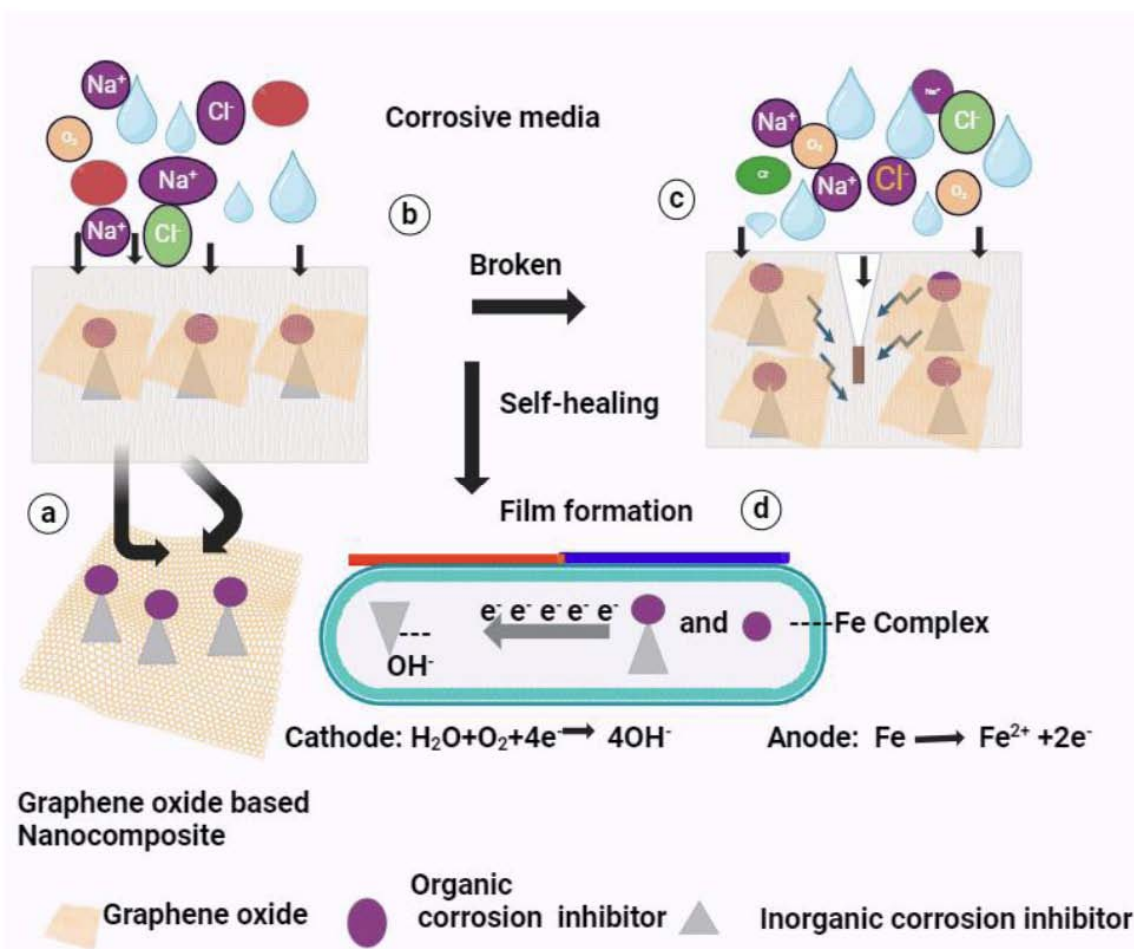
coatings, which are (1) graphene derivative selection, (2) nanocomposite matrix composition, (3) nanofiller dispersion concentration, (4) environmental conditions, (5) testing and evaluation methods. It is imperative to consider and evaluate all these factors collectively in the design of new graphene derivatives for effective self-healing, anti-corrosion, and anti-biofouling properties.

#### 4.2. Anti-Corrosion Coatings Involving Functionalized GO

Table 1 summarizes recent studies of using GO and/or f-GO hybrid materials to improve the anti-corrosion performance of organic coatings. The following discussion is organized according to the types of functional materials combined with GO and f-GO.

##### 4.2.1. Graphene and Silane Coupling Agents

Pourhashem *et al.* in 2017 investigated the corrosion protection mechanism of nanocomposites made of f-GO with two silane coupling agents, namely 3-aminopropyltriethoxysilane (APTES) and 3-glycidoxypropyltrimethoxysilane (GPTMS), in epoxy resin [66]. Their studies showed that the OH groups in GO sheets formed Si-O-Si bonds with the



**Figure 3:** Schematically illustration of (a) GO-based nanocomposite, (b) corrosion initiation, (c) release of corrosion inhibitors, (d) protecting-film formation through self-healing inhibition mechanism for anti-corrosion coatings.

**Table 1: Recent Studies of Graphene Derivative-Based Nanocomposites for Anti-Corrosion Coatings**

Author (Year)	GO Derivatives Applied	Outcomes
Pourhashem <i>et al.</i> (2017)	GO, aminopropyltriethoxysilane (APTES), 3-glycidyloxypropyl trimethoxysilane (GPTMS), and epoxy resin.	Amine end group functionalized GO afforded more corrosion resistance.
Deghani <i>et al.</i> (2022)	GO, grafted L- citrulline (LC) loaded beta-cyclodextrin, APTES, epoxy resin.	Significantly decreased corrosion current and increased total resistance.
Rameznzadeh <i>et al.</i> (2016)	GO, aminosilane, 1-4 butanediol glycidyl ether (BDDE)	A mixture of modified nano clay and modified GO (MNC-MGO, 30:70wt%) significantly improved corrosion resistance compared to MGO and MNC alone.
Javidparvar <i>et al.</i> (2020)	GO, benzimidazole (BI), cerium ions (Ce), epoxy	Layer formation at cathodic and anodic sites was responsible for superior corrosion protection and self-healing properties.
Vinodhini <i>et al.</i> (2021)	f-GO, 3-amino-1,2,4- triazole -5- thiol (ATT)	Significant enhancement in charge transfer resistance, film resistance, and reduced capacitance.
Li <i>et al.</i> (2021), Majidi <i>et al.</i> (2023)	GO, zeolitic imidazolite framework (ZIF), mercaptobenzimidazole	Improvement in compatibility and crosslinking density with polymer matrix. The fabricated nanocomposite showed charge transfer resistance six times greater than neat epoxy.
Gao <i>et al.</i> (2023)	f-GO, amorphous cellulose (AC), waterborne epoxy resin (WEP)	2.0wt% NAC/NGO@EP achieved an impedance value ( $8.955 \times 10^8 \Omega \text{ cm}^2$ ) 3 times higher than pure epoxy.
Askarnia <i>et al.</i> (2022)	GO, hydroxyapatite, chitosan, epoxy resin	Corrosion rate decreased from 4.3 to 0.2 (mpv) with increasing GO concentration up to 2%.
Mostafatabar <i>et al.</i> (2022)	GO flakes, polydopamine (PDA), chitosan, zinc ion ( $\text{Zn}^{2+}$ ), epoxy resin	GPCZ (GO-PDA-CS-Zn) showed 90% protection against delamination and degradation.
Khosravi <i>et al.</i> (2023)	GO, molybdate (MO), PDA	The fabricated composite showed a 91% corrosion mitigation index and 88% corrosion inhibition.
Deghani <i>et al.</i> (2022)	GO, echium ammonium extract (EAE), epoxy resin	Efficient corrosion inhibition due to the formation of chelation complexes between EAE molecules and Fe atoms.
Kumar <i>et al.</i> (2020)	Graphene sheets, Zn, Ni, Fe	Composites containing a high proportion of graphene and Fe showed superior corrosion protection performance.
Ye <i>et al.</i> (2020)	Graphene sheet, porous polyhedral oligomeric silsesquioxane (POSS), benzotriazole (BTA), epoxy resin	8-PG-BTA/EP showed the least water absorption capability.

silane agents. The aliphatic chains of organosilanes reduced the hydrophilicity of GO nanosheets. The aliphatic chains in GPTMS-GO are much longer than those in APTES-GO, making it more hydrophobic than the other. These silane-modified GO derivatives formed covalent Si-O-metal bonds between the silane and the surface metal hydroxyl in the epoxy coating, which ultimately increased the density of linkage between the coating and the substrate. Such effects reduced the delamination of coating in the presence of corrosive agents.

Furthermore, the f-GO nanosheets improved the interfacial bonding strength with the polymer matrix through covalent bonding between f-GO and polymer during the curing process, resulting in increased crosslinking density of the polymer coating. The APTES-GO contains amino functional groups, which are more active in forming hydrogen bonding with the glycidyl groups of the epoxy polymer. This property led to improved corrosion protection as well.

#### 4.2.2. Graphene and Organic/Inorganic Corrosion Inhibitors

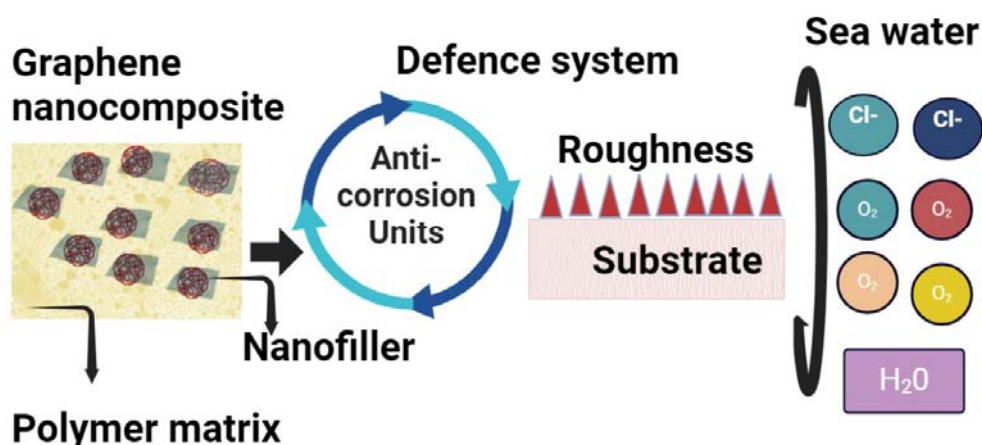
Javidparvar and co-workers recently (2020) combined GO with benzimidazole (BI) and cerium ions (Ce) to form

functional nanocontainers for anti-corrosion application [67]. The fabricated nanocontainers (GO/Ce-BI) were added to an epoxy coating and achieved enhanced film barrier properties and corrosion protection efficiency. They reported that the synergistic effects of Ce/BI-decorated GO sheets gave rise to improved coating self-healing function and anti-corrosion performance under both intact and defective conditions. Whenever the coating experiences damage, the formation of a cerium oxide/hydroxide layer at the cathodic area may reduce the pH and inhibit the detachment of the steel-coating bonds. Moreover, the formation of a layer with the composition of cerium oxide/hydroxide and Fe-BI/Ce-BI complexes at the anodic area was found to be responsible for the corrosion protection superiority and self-healing properties. Figure 4 illustrates how these anti-corrosion units act together to form a defense system that significantly hinders the penetration of water, oxygen, and other corrosive agents, thereby protecting the underlying metal surfaces from corrosion.

#### 4.2.3. Graphene and Pigments

In 2021, Vinodhini and Xavier introduced a nanocomposite made of f-GO and 3-amino-1,2,4-triazole-5-thiol (ATT) as an





**Figure 4:** Schematic illustration of the anti-corrosion effects of GO nanocomposite in coatings.

advantageous pigment for improving the protective properties of polymer coatings [68]. Electrochemical impedance spectroscopic (EIS) studies revealed that the addition of this f-GO-ATT pigment in organic coatings led to significantly enhanced charge transfer resistance and film resistance, as well as reduced capacitance. Scanning electrochemical microscopic (SECM) analysis showed less current distribution (0.5-2.5 I/nA) at the scratched surface of f-GO-grafted composite coatings compared to neat epoxy coatings (2-10 I/nA) on mild steels. The presence of sulfur and nitrogen atoms in the f-GO is believed to facilitate the corrosion protection of the epoxy-f-GO-coated mild steel.

#### 4.2.4. Graphene and Metal-Organic Frameworks (MOFs)

In 2021, Li *et al.* developed a sophisticated anti-corrosion coating material by combining 2-mercaptobenzimidazole (M) into zeolitic imidazolate framework-8 (ZIF-8) with GO nanosheets [69]. This composite was applied with an epoxy resin (EP) to produce an anti-corrosion coating showing pH-responsive and self-healing properties. EIS analysis revealed that the M-ZIF-8/GO/EP coating gave outstanding self-healing capabilities, attributable to the release of corrosion inhibitors to form a protective film on the metal surface. With these properties, the coating containing M-ZIF-8/GO composite achieved impressive anti-corrosion performance. The M-ZIF-8/GO system could react with the epoxy resin, significantly improving their compatibility as well as the crosslinking density of the epoxy coating.

In 2023, Majidi *et al.*, through modification of GO with nickel/2-methylimidazole (Ni-MOF), produced a GO nanocarrier as a pH-controlled release system, where 2-mercaptobenzothiazole (MBT) was loaded as a corrosion inhibitor [70]. Their studies based on EIS analysis indicated that the charge transfer resistance of an epoxy coating blended with this GO nanocomposite was approximately six times greater than that of the neat epoxy. This superior protection and self-healing ability can be attributed to the blocking effect of the GO/MOF system, the excellent compatibility of GO and MOF, and the synergistic effect of the Ni-MOF particle and MBT corrosion inhibitor that can release

corrosion inhibitor and provide corrosion protection film via a pH-responsive mechanism.

#### 4.2.5. Graphene and Natural Polymers

In 2023, Zhang *et al.* fabricated a compact structure made of amorphous cellulose (AC) and GO through electrostatic self-assembly of negatively charged AC (NAC) and positively charged GO (PGO) [71]. Different amounts of NAC/PGO were then mixed with waterborne epoxy resins (WEP). The resulting coating (2.0wt%NAC/NGO@EP) showed an impedance value ( $8.955 \times 10^8 \Omega \text{ cm}^2$ ) at a low frequency three times higher than that of pure epoxy resin. Their studies also suggested that several factors, such as good dispersity and interfacial compatibility, were responsible for significantly enhanced corrosion protection performance of the WEP coating.

#### 4.2.6. GO and Bio-Polymers

In 2022, Mostafatabar *et al.* developed an innovative strategy for surface modification of GO flakes with biocompatible materials based on polydopamine (PDA) and chitosan (CS) [72]. To this composite material, the Zn (II) ion was loaded as a corrosion inhibitor, and the resulting nanocomposite was applied to epoxy coatings for enhanced anti-corrosion properties. Their studies demonstrated that the corrosion inhibitive species ( $\text{Zn}^{2+}$ ) could be released from the GPCZ (GO-PDA-CS-Zn) coating through pH control, pointing to a suitable approach for self-healing performance. They also examined the barrier and active corrosion protection properties of the nanocomposites. It was found that the coating could achieve 90% protection efficiency against coating degradation and delamination, along with self-healing performance.

In 2022, Askarnia *et al.* synthesized a ternary hydroxyapatite/chitosan/GO (HA/CS/GO) coating through an electrophoretic deposition method on magnesium alloys [73]. The impact of GO on corrosion behavior and antibacterial properties of the composite coating was examined. The results of their study indicated that the rate of corrosion could be significantly decreased from 4.3 to 0.2 (mpy) when the amount of GO was

increased from 0 to 2 wt% due to the reduction of the surface cracks.

In 2023, Khosravi and collaborators developed an epoxy composite coating with a dual-barrier-active self-healing capability for anti-corrosion purposes [74]. Their method involved the treatment of GO nanosheets with polydopamine (PDA) and molybdate (MO) ions as organic and inorganic hybrid inhibitors, respectively. The investigation was focused on understanding the release kinetics of PDA and MO from the GO nanosheets. EIS analyses demonstrated an inhibition efficiency of 88% for the sample immersed in the solution containing GO/PDA/MO after 48 hours. Polarization results indicated a corrosion mitigation index of 91% for the sample submerged in the extract of GO/PDA/MO after 48 hours. This study also elucidated that the designed GO/PDA/MO-epoxy coating effectively curtailed metallic substrate corrosion through two mechanisms. The first one is due to the enhancement of the diffusion pathway of electrolytes (barrier mechanism), and the second one is based on active protection against corrosion by releasing the loaded inhibitors in the corroded areas (self-healing mechanism).

#### 4.2.7. Graphene and Materials from Natural Sources

In 2022, Deghani *et al.* developed an anti-corrosion nanocomposite epoxy (EP) coating based on GO nanoparticles modified by echium ammonium extract (EAE) [75]. Their results revealed that EAE in EP enriched the barrier function and formed a protective layer inside the scratch, which led to a self-healing function. When the coating experiences damage, a protective film on the substrate in the defective zone is formed, and the self-healing effect provides corrosion protection to retard the metal dissolution. Moreover, the presence of modified GO nanolayers in the epoxy coating not only enhanced the barrier function but also delivered EAE molecules to the anodic zones of the steel surface. The EAE molecules

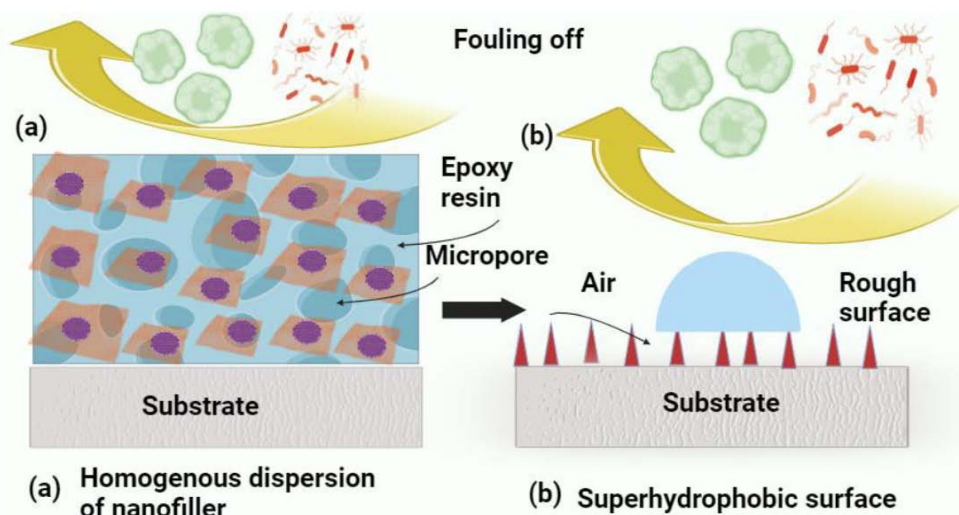
adsorbed on the active anodic zones also contribute to corrosion protection. In a sense, corrosion protection was enhanced through active inhibition of the anodic zones and the formation of chelation complexes between EAE molecules and Fe atoms.

#### 4.2.8. Graphene and Metal Species

In 2020, Kumar and colleagues investigated ZnNiFe-graphene composite coatings, focusing on their composition, morphology, and corrosion behavior [76]. Through potentiodynamic polarization and EIS analyses, they concluded that graphene could induce notable changes in the surface morphology of the coating and elevate the concentration of Ni, consequently improving the corrosion resistance of the ZnNiFe-graphene composite coating. The composite coating with the highest proportions of graphene and Ni was found to have superior corrosion resistance performance. This outcome was attributed to the increased compactness of the coating and the reduction of micropores, as well as surface defects.

#### 4.3. Graphene Derivative-Based Nanocomposites in Anti-biofouling/Antimicrobial Coatings

Apart from anti-corrosion, the application of graphene-based nanocomposites in anti-biofouling/antimicrobial coatings has been actively pursued in recent years. Figure 5 illustrates how the dispersion of nanoparticles into a polymer matrix can give rise to increased hydrophobicity and surface roughness, which could further contribute to enhanced resistance against microorganism attacks. This type of antifouling coating is particularly useful for application in marine environments, where biofouling significantly impacts the hydrodynamics of ship hulls, leading to increased drags and fuel consumption as well as maintenance costs. GO's inherent antimicrobial properties can enhance the coating's resistance to microbial accumulation and growth. The use of GO in antifouling



**Figure 5:** Schematic illustration of factors: (a) homogenous dispersion of nanofiller, and (b) superhydrophobic surface affecting the antifouling effects of GO nanocomposite in coatings.

coatings not only extends the lifespan of marine vessels and infrastructure but also saves operational costs and lowers their environmental impacts by decreasing the need for toxic biocidal agents traditionally used in coatings. Essentially, GO is a promising material for sustainable and high-performance antifouling technology. Recent research has focused on developing practical and environmentally friendly fouling release coatings (FRC), particularly those based on silicone. PDMS paints have been proven to be highly effective on fast-moving vessels, utilizing dynamic forces generated by vessel movement to release accumulated organisms due to the vessel surface's low surface energy and elastic modulus. However, these coatings show limited effectiveness on slow-moving vessels such as installed sensors and aquaculture nets. PDMS/nano-filler nanocomposite materials have been created to increase resistance against microorganism attacks. Recent studies of antifouling polymeric coatings that involve the use of graphene and other functional materials are summarized in Table 2. The following discussion is organized according to the type of functional materials in combination with different graphene derivatives.

#### 4.3.1. Graphene and Metal Oxide Nanoparticles

Graphene derivatives such as GO contain different oxygen functional groups and polyaromatic units in their structures. These functional groups allow the attachment of metal and metal oxide nanoparticles (NPs) to GO through various interactions, for example, cation- $\pi$ -type interactions and metal-oxygen bonding. GO is an excellent dispersant and carrier of NPs, while GO-NP nanocomposites are promising candidate materials in the field of antifouling application. NPs can serve as nanofillers in a polymer matrix, boosting the antifouling properties of the resulting nanocomposites. Owing to their outstanding physicochemical characteristics, biocompatibility, and antimicrobial activity, graphene-based nanocomposites have found increasing application in anti-biofouling coatings.

Zhang and co-workers in 2021 prepared a type of ZnO-GO material through a facile one-pot reaction [77]. The resulting ZnO-GO composite was further blended into a polydimethylsiloxane (PDMS) matrix in varied amounts using a simple solution mixing method to form PDMS/ZnO-GO nanocomposites (PZGO). The hydrophobicity, surface roughness (Ra), surface free energy (SFE), and nanoscale

structure of these nanocomposites were examined through surface and morphological analyses. Antifouling tests were conducted with two marine microorganisms, the cyanobacterium *Synechococcus sp. Strain PCC 7002* and the diatom *Phaeodactylum tricornutum*. The results of antifouling tests indicated that PZGO 0.2 (mass ratio of ZnO-GO to PDMS: 0.2 wt%) exhibited outstanding antifouling properties with 8.5% coverage of *Synechococcus sp. strain PCC 7002* biofilm. Additionally, PZGO 0.1 (mass ratio of ZnO-GO to PDMS: 0.1 wt%) demonstrated a 2.4% coverage of *P. tricornutum biofilm*. The study also disclosed that the mass ratio of PZGO in coatings is an essential factor in efficient antifouling performance.

Balakrishnan and co-workers in 2020 reported a GO-silica-polydimethylsiloxane (GSP) coating, which demonstrated excellent anti-corrosion and anti-biofouling performance on carbon steel [78]. Electrochemical analyses of the GSP-coated carbon steel exposed to Gram-positive *Bacillus sp.* or Gram-negative *Pseudomonas sp.* and freshwater bacterial cultures for 72 hours showed a significant reduction in corrosion current ( $i_{corr}$ ) by 3-5 orders of magnitude and high impedance values ( $10^7 \Omega$ ) compared to uncoated specimens. The corrosion protection efficiency of GSP-coated specimens reached 99.9% against *Bacillus sp.* and freshwater culture and 89.6% against *Pseudomonas sp.* Microbiological and microscopic analyses showed superior anti-corrosive and anti-biofouling properties of the GO composite coating. The defect-free coating of GO with polydimethylsiloxane (PDMS) also provided enhanced resistance against bacterial attacks and microbially induced corrosion (MIC). Moreover, this type of coating is environmentally friendly and can potentially be used to prevent pipeline materials in cooling water transport from microbial corrosion and biofouling.

#### 4.3.2. Graphene and Boehmite Nanorods

In 2022, Selim *et al.* reported two series of superhydrophobic nanocomposites for maritime fouling-release (FR) coatings [79]. These nanocomposites are made of polydimethylsiloxane (PDMS) enriched with rGO and GO/boehmite nanorods (GO- $\gamma$ -AlOOH) as nanofillers. The synthesis was done through a hydrothermal method for rGO and a chemical deposition method for GO- $\gamma$ -AlOOH. The researchers explored the self-cleaning and antifouling properties by controlling the structures and distribution of the nanofillers in

**Table2: Recent Studies of Graphene Derivative-Based Nanocomposites for Anti Fouling Coatings**

Author (Year)	Coating Materials Used	Outcomes
Zhang <i>et al.</i> (2021)	ZnO-GO, polydimethylsiloxane (PDMS)	Outstanding antifouling properties against <i>Synechococcus sp. strain PCC 7002</i> and <i>P. tricornutum</i> .
Balakrishnan <i>et al.</i> (2020)	GO, silica, polydimethylsiloxane	The corrosion protection efficiency reached 99.9% against <i>Bacillus sp</i> and 89.6% against <i>Pseudomonas species</i> .
Selim <i>et al.</i> (2022)	PDMS, GO, $\gamma$ -AlOOH	Attained the lowest biodegradability (1.6%) and microbial endurance for Gram-positive and Gram-negative bacteria and fungi at 86.42%, 97.94%, and 85.97%, respectively.
Selim <i>et al.</i> (2024)	PDMS, PMMA, Ag, TiO <sub>2</sub> , GO	The fabricated composite showed super hydrophobicity, surface roughness, and low surface free energy.

the silicone matrix. The nanofillers were dispersed in the silicone matrix using the solution casting method, and they examined the synergistic effects of the nanocomposites on surface, mechanical, and FR characteristics. Water contact angle (WCA) measurement, scanning electron microscopy (SEM), and atomic force microscopy (AFM) were employed to analyze the hydrophobicity and antifouling properties of the surface. The nanocomposite's roughness, super hydrophobicity, and surface mechanical properties demonstrated improvement with homogeneity in nanofiller dispersion. Laboratory assessments were conducted over 30 days using selected microorganisms to evaluate antifouling effects. Their results showed that the PDMS/GO- $\gamma$ -AIOOH nanorod composite had superior antibacterial activity compared to the PDMS/rGO nanocomposite against various bacterial strains. The performance was attributed to the high surface area and stabilizing effects of the GO- $\gamma$ -AIOOH hybrid nanofillers. The PDMS/GO- $\gamma$ -AIOOH nanorod composite (3 wt%) exhibited the lowest biodegradability percentage (1.6%), and the microbial endurance percentages for Gram-positive, Gram-negative, and fungi were 86.42%, 97.94%, and 85.97%, respectively. A 45-day field trial in natural seawater was also carried out, confirming the good FR performance of the coating.

#### 4.3.3. Graphene and Metal/Metal Oxide Nanoparticles

In 2024, Selim and co-workers developed a novel marine coating for ship hulls that is non-toxic and non-sticking (i.e., superhydrophobic) [80]. They employed a catalytic hydrosilylation method to graft Ag nanospheres and TiO<sub>2</sub> nanorods onto the structure of GO, forming a composite known as Ag-TiO<sub>2</sub>@GO. To create effective antifouling coatings, various proportions of Ag-TiO<sub>2</sub>@GO nanofillers were incorporated into a matrix of PDMS-PMMA. The PDMS-PMMA/Ag-TiO<sub>2</sub>@GO nanocomposite with a 2.5 wt% concentration of nanofillers was found to exhibit superior superhydrophobicity (with a water contact angle of  $160 \pm 2^\circ$ ), significant surface roughness (103.4 nm RMS), and the lowest surface free energy (22.9 mN/m). Higher nanofiller concentrations (up to 5 wt%) actually resulted in reduced water and fouling repellency and increased surface energy due to increased particle clustering. Notably, the composite demonstrated non-toxicity when tested against *Trichogaster lalius* fish and the bivalve *Brachidontes variabilis* model species. It also exhibited the lowest biodegradability percentages and optical density against different bacterial strains.

## 5. RECENT PROGRESSES IN THIN-FILM ELECTROCHEMICAL SENSORS BASED ON GRAPHENE DERIVATIVES

Incorporating graphene and graphene derivatives in conducting polymer matrices has proven to be an effective strategy to improve significantly the performance of thin-film electrochemical sensors and sensor arrays. The beneficial effects of graphene and graphene derivatives mainly arise

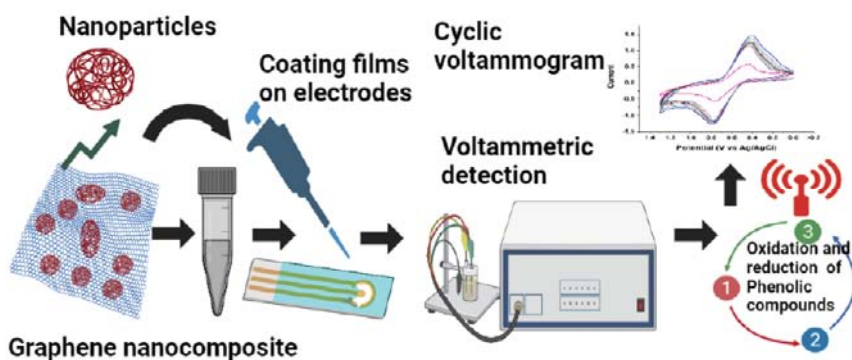
from the high conductivity, stability, and large surface area of graphene, which facilitate the electrochemical sensing materials to attain higher sensitivity, lower detection limit, longer operational lifetime, and reproducibility. Graphene derivatives such as GO and rGO contain defects in their structures, which can deliver synergistic electrocatalytic effects along with other electroactive components to bring about desired selectivity for specific analytes.

Reviews of advancements in graphene-based electrochemical sensors have been made by several recent publications, most of which are focused on biosensing applications. In the field of environmental science and engineering, efficient methods for detecting emerging organic pollutants have received growing attention [81]. Among numerous organic pollutants, phenolic compounds are one of the main contributors to water source contamination, coming from various natural and anthropogenic sources. As phenolic compounds are highly toxic, slow to degrade, and prone to bioaccumulation, posing significant health and environmental risks, it is essential to monitor and detect these pollutants accurately [82]. Phenolic compounds encompass a wide range of structures, ranging from simple phenols to complex polyphenols. This structural diversity makes it difficult to develop a single detection method that works for all phenolic compounds.

Consequently, accurate identification and quantification of phenolic pollutants in the environment often rely on sophisticated and expensive analytical techniques like HPLC-MS or LC-MS/MS. However, these traditional methods are usually time-consuming, labor-intensive, and expensive. Even at low concentrations, many phenolic compounds are toxic to humans and other organisms. Long-term exposure to them can cause serious health issues like irregular breathing, muscle weakness, and respiratory arrest at lethal doses. Therefore, rapid and cost-effective detection/sensing methods for various phenolic pollutants are critically needed in recent years. They can serve as early warning systems, allowing for faster response to potential health threats and timely remediation measures to be deployed when accidental release of phenols occurs in industrial activities.

Electrochemical sensors are a versatile and widely used technology for detecting gases, pollutants, and biological compounds across various applications, owing to their advantages in terms of fast response time, low power requirements, compact sizes, cost-effectiveness, and easy integration with other analytical methods. Recent studies have demonstrated that graphene derivatives offer a promising solution for the development of efficient electrochemical sensors for phenolic compounds. Figure 6 illustrates the synthetic process of graphene sheets modified with nanoparticles, which are incorporated into polymer matrices and used to modify electrode surfaces for fabricating electrochemical sensors. With suitable modification and





**Figure 6:** Schematic illustration of the GO nanocomposite application in the fabrication of coating film on electrodes.

tuning of the GO-based sensing materials, this type of sensor can exhibit high sensitivity and effective adsorption of phenolic compounds.

### 5.1. Electrochemical Sensors Enabled by Composites of Graphene and MOFs

In 2022, Tang *et al.* ultrasonically treated graphene (Gr) with a zirconium MOF, known as UiO-66, to obtain a Gr-UiO-66 composite [83]. This composite was further combined with magnetic molecularly imprinted polymer (mag-MIP) and then applied onto the surface of a screen-printed electrode (SPE). This fabricated mag-MIP/Gr-UiO-66/SPE sensor showed good selectivity for cannabidiol (CBD). Under optimal conditions, the mag-MIP/Gr-UiO-66/SPE sensor detected CBD with enhanced electrochemical signals. It has been found that such modified electrodes have reasonable practicability for actual samples in comparison to traditional analytical methods. Based on their results, the sensors were considered to have great potential in detecting natural active compounds in the food, pharmaceutical, cosmetic, and healthcare industries.

In 2021, Yu *et al.* constructed microporous resorcin[4]arene based MOF materials and successfully immobilized them on GO to form a Mn-MOF@GO composite [84]. Further, through the electrochemical reduction of GO at a high negative potential, they obtained a composite material, Mn-MOF@rGO. The results of their study showed that the glassy carbon electrode (GCE) coated with Mn-MOF@rGO featured electrochemical activity for the reduction of nitrophenol isomers, owing to the improved conductivity of the composites. Moreover, it was reported that a Mn-MOF@rGO/GCE composite gave simultaneous sensing of *p*-NP (*p*-nitrophenol) and *o*-NP (*o*-nitrophenol) in a wide linear range and a low limit of detection (LoD).

### 5.2. Electrochemical Sensors Enabled by Composites of Graphene and Metals/Metal Oxides

Wang *et al.*, in 2023, developed a green synthetic strategy to determine *p*-NP through an electrodeposition method [85]. In their method, rGO and nickel selenide ( $\text{Ni}_3\text{Se}_4$ ) were successively applied onto the surface of indium tin oxide (ITO) glass. They reported that the presence of nickel

selenide effectively inhibited the stacking of graphene lamellas and, hence, improved the electrical conductivity of the composites. The results of their study demonstrated that the  $\text{Ni}_3\text{Se}_4/\text{rGO}/\text{ITO}$  electrode worked as an efficient electrochemical sensor for phenols, with high selectivity, remarkable reproducibility, and good stability. The excellent sensor performance could be attributed to the synergistic effects due to the combination of rGO and  $\text{Ni}_3\text{Se}_4$ . Overall, this study provided a promising solution for rapid and selective monitoring of organic phenolic pollutants in actual water samples.

In 2023, Liu *et al.* developed a laser-induced method for synthesizing manganese oxide/reduced graphene oxide (MnOx/rGO) composites, which were then applied to modify screen-printed electrodes (SPE) [86]. The carboxyl groups in GO attracted manganese ions in the precursor solution, ensuring their uniform dispersion across the graphene surface. This structural design minimized electron-transfer distances and hence enhanced the electrocatalytic properties of the modified SPE. Simultaneous detection of two dihydroxybenzene isomers, hydroquinone (HQ) and catechol (CC), was demonstrated with this electrochemical sensor. Cyclic voltammetric (CV) analysis showed that their electrochemical activity is in the potential range of -0.2 to 0.6 V. Linear response ranges from 0.5 to 200  $\mu\text{M}$ , with limits of detection (LoD) at 0.049  $\mu\text{M}$  for HQ and 0.028  $\mu\text{M}$  for CC.

In 2023, Liao *et al.* produced a composite of nickel/nitrogen-doped graphene oxide (Ni/N-GO) using a high-temperature thermal reduction approach [87]. This composite was applied to modify a glassy carbon electrode (GCE), creating an electrochemical sensor denoted as Ni/N-GO/GCE. This sensor was designed explicitly to selectively detect catechol (CC) and hydroquinone (HQ). Under optimal conditions, the electrochemical sensor exhibited outstanding catalytic performance in the redox reactions of CC and HQ. The outcomes demonstrated that Ni/N-GO/GCE served as a promising electrode, showcasing remarkable long-term stability and reproducibility for the determination of hydroquinone isomers.

In 2023, Nawaz *et al.* synthesized a composite of Zn and rGO by a straightforward microwave-assisted method [88]. This



ZnO/rGO composite was then used to fabricate a ZnO/rGO-modified glassy carbon electrode (ZnO/rGO/GCE) for selective and trace-level determination of 2,4,6-trichlorophenol (TCP) in aqueous environments. The conductivity and electrocatalytic properties of ZnO/rGO/GCE were assessed using various electrochemical methods. The results revealed that the ZnO/rGO/GCE achieved a limit of detection (LoD) and limit of quantification (LoQ) for TCP at 0.0067  $\mu\text{M}$  and 0.019  $\mu\text{M}$ , respectively. Additionally, the anti-interference characteristics and stable performance of ZnO/rGO/GCE establish this proposed electrochemical sensor as an excellent tool for accurately measuring TCP in environmental water samples.

Kalia and colleagues in 2024 synthesized a ternary nanocomposite material, rGO–molybdenum disulfide/iron oxide (rGO–MoS<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>), through a microwave irradiation method [89]. In this process, the layered structure of rGO nanosheets served as a substrate for molybdenum disulfide (MoS<sub>2</sub>) on their surface. At the same time, iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were incorporated to enhance the conductivity of the resulting nanocomposite. The heightened conductivity contributed to an increased sensitivity for detecting *p*-NP. Cyclic voltammetric analyses indicated that the rGO–MoS<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>-modified glassy carbon electrode exhibited a 170% rise in current compared to the bare electrode. The limit of detection (LoD), limit of quantification (LoQ), and sensitivity, as determined through differential pulse voltammetry studies, were found to be 0.8  $\mu\text{M}$ , 2.46  $\mu\text{M}$ , and 0.71  $\text{mA mM}^{-1} \text{cm}^{-2}$ , respectively. Raman spectroscopic analysis of the nanocomposite revealed an increase in the intensity of the D band compared to rGO, indicating the introduction of non-graphitic defects due to the presence of Fe<sub>3</sub>O<sub>4</sub> and MoS<sub>2</sub>. This research demonstrated the potential of carbon and transition metal dichalcogenide nanocomposites in this field as opposed to metal-based nanoparticles.

### 5.3. Electrochemical Sensors Enabled by Composites of Graphene and Biomaterials

Wang *et al.*, in 2023, investigated the electrochemical sensing properties of a composite made from graphene oxide/cellulose nanofibrils (GO/CNF). This composite was applied to generate a modified carbon paste electrode, GO/CNF/CPE, which turned out to be helpful for the precise and dependable detection of *p*-NP in water samples based on differential pulse voltammetry (DPV) and cyclic voltammetry (CV) analyses [85]. The advantageous features of this type of sensor include fast response time, good selectivity, high sensitivity, and accuracy. The improved sensing performance was attributed to a fast electron transfer rate that makes the electrochemically active surface area of the electrode show enhanced catalytic activity. Under optimal conditions, the analyte's peak current displayed a broad linear correlation with its concentration within the range of 3.0 nM–210  $\mu\text{M}$ , achieving a low limit of detection (LoD) value of 0.8 nM.

### 5.4. Electrochemical Sensors Enabled by Composites of Graphene and Organic Conjugated Molecules

Jia *et al.*, in 2023, synthesized a type of pyridine diketopyrrolopyrrole-functionalized graphene oxide (PDPP–GO) composite material through a straightforward reaction in an aqueous solution [90]. The results of physical and chemical characterizations indicated a tight integration of PDPP with GO assembled through  $\pi$ – $\pi$  stacking and robust hydrogen bonding. This synthetic method effectively addressed both the electrical conductivity issue of GO and the solubility concern of PDPP, opening new possibilities for combining with other materials in aqueous solutions. Particularly noteworthy is that the composite could be used to effectively modify a glassy carbon electrode, resulting in a PDPP–GO/GCE electrochemical sensor. Studies showed that this sensor exhibited outstanding electrocatalytic activity for detecting *p*-NP, displaying higher sensitivities of 18.54 and 6.61  $\text{mA mM}^{-1} \text{cm}^{-2}$  compared to other sensors based on GO. The sensor performance was further validated by the detection of *p*-NP in real samples, demonstrating comprehensive sensing performance that aligns perfectly with the requirements for modern electrochemical sensors. The aforementioned electrochemical sensors based on graphene derivatives are summarized in Table 3.

## 6. CONCLUDING REMARKS, CHALLENGES, AND FUTURE PERSPECTIVES

This review article provides a glimpse at the most recent progress in the application of graphene derivatives in fabricating nanocomposites with multifunctional capabilities, such as self-healing anti-corrosion coatings, anti-biofouling coatings, as well as high-performance electrochemical sensors for environmentally critical phenolic compounds. Our literature survey has clearly demonstrated that graphene derivatives are versatile and functional materials with broad applicability in the fields of coating and thin-film sensing technologies. The outstanding electrical conductivity, mechanical strength, high surface area, and rich electrochemical redox activities of graphene and graphene derivatives serve as the main driver for the ongoing research in graphene-based nanocomposite materials. On the other hand, the interplays between graphene and other advanced functional nanomaterials, such as conductive polymers, molecular frameworks, and metal/metal oxide nanoparticles, have been demonstrated to be highly valuable in the design of novel material functions. Continued studies in this direction should disclose more opportunities for graphene-based materials and technologies. An important forefront in this field of research is focused on taking advantage of the green (environmentally friendly) aspect of graphene derivatives. Therefore, it is expected that graphene-derived nanocomposites will offer practical solutions to many challenging research topics within the framework of sustainable materials and energies in the years to come. Obviously, a key challenge facing the development of various

**Table3: Summary of Recent Progress in Electro Chemical Sensors for Phenols using Grapheme Derivatives as the Active Sensing Components**

Author (Year)	Materials Used	Outcomes
Tang <i>et al.</i> (2022)	Zr-MOF (UiO-66), Gr, and MIP on SPE	Good selectivity and adsorption of CBD.
Yu <i>et al.</i> (2021)	Resorcin[4]arene-MOF, rGO, and Mn on GCE	Simultaneous detection of <i>p</i> -NP and <i>o</i> -NP in a wide linear range and lower limit of detection.
Wang <i>et al.</i> (2023)	Ni <sub>3</sub> Se <sub>4</sub> and r-GO on ITO glass	Excellent selectivity, reproducibility, and stability
Liu <i>et al.</i> (2023)	MnOx/r-GO on SPE	Simultaneous detection of HQ and CC.
Liao <i>et al.</i> (2023)	N-doped GO and Ni on GCE	Highly selective detection of HQ and CC.
Nawaz <i>et al.</i> (2023)	ZnO and r-GO on GCE	Selective detection of trace 2,4,6-TCP in an aqueous environment.
Wang <i>et al.</i> (2023)	Cellulose nanofibrils and GO on CPE	High sensitivity, selectivity, and accuracy in analyzing real samples containing <i>p</i> -NP.
Jia <i>et al.</i> (2023)	PDPP-GO on GCE	Outstanding electrocatalytic activity for detecting <i>p</i> -NP with high sensitivities of 18.54 and 6.61 mA mM <sup>-1</sup> cm <sup>-2</sup> .

graphene-based technologies is to establish more cost-effective and scalable production methods for functional graphene derivatives so that their application in industrial sectors can be technically and economically feasible.

For long-term active corrosion protection performance, integration of graphene derivatives into polymer matrices is critical. How to achieve uniform dispersion of graphene derivatives within polymer matrices can be challenging. Agglomeration issues arising from graphene sheets may impact the overall performance and mechanical durability of the nanocomposite. Therefore, a proper understanding of the long-term stability and durability of graphene-based nanocomposites in real-world environments, especially under varying temperatures, humidity, salinity, and exposure conditions, is critical for their practical deployment. Moreover, thorough investigations of their potential toxicity and their environmental impact assessment of associated risks to human health or the ecosystem of graphene-based nanocomposite is quite challenging. Henceforth, standardized testing methods and regulations for graphene-based nanocomposites pose challenges for their widespread commercial use. Establishing industry standards and regulations is essential for ensuring product quality and safety in the future. Another promising direction that deserves significant attention is the incorporation of graphene-based nanocomposites into innovative coatings that possess sensing abilities for real-time monitoring of corrosion, structural integrity, and environmental conditions. It holds exciting possibilities, ranging from advanced materials with tailored properties to transformative applications in diverse industries. Continued research, technological breakthroughs, and collaborative efforts will drive the evolution of these materials and expand their role in shaping the future of materials science and technology.

Future research will likely be focused on addressing environmental concerns associated with graphene derivatives, ranging from developing sustainable production methods, conducting thorough life-cycle assessments, and

exploring eco-friendly disposal options. These will be essential for the responsible use of these materials. Further advancements will benefit from increased global collaborations and interdisciplinary research efforts. Bringing together experts from materials science, chemistry, physics, engineering, and other fields will accelerate innovations and open new avenues for graphene derivative-based nanocomposites. Addressing these challenges and exploring these future perspectives will contribute to unlocking the full potential of graphene derivative-based nanocomposites and expanding their applications across various industries.

Our analysis of the literature has shown that nanocomposites with multifunctional capabilities can be created by modifying the surfaces of various graphene derivatives, including GO, rGO, and graphene sheets, with inorganic, organic, biopolymer, MOF, and nanoporous materials. Adjustment of surface properties such as hydrophobicity, surface free energy, roughness, and hierarchical micro-/nanostructure allows for customization, resulting in unparalleled antifouling performance. It is crucial to increase the water contact angle of the coating surface, enhance bonding strength to metallic substrates, and improve interfacial bonding strength and crosslinking density during the polymer coating curing process to achieve superior barrier anti-corrosion performance. The introduction of self-healing properties in nanocomposites requires effective ligands to form durable complexes with metallic cations, along with corrosion-inhibiting agents that induce passivation and chelation effects to halt anodic and cathodic reactions.

For the electrochemical activity of graphene-based nanocomposites, considerable research efforts have already been made, but much work is still required to broaden their scope and bring their practical application to the future. To overcome the current challenges, such as exploring the facile route of synthesis, functionalization, and controlled processing of GO derivative-based nanocomposites it is important to gain deeper understanding of the effect of defects on the GO conductivity, rapid electron transfer kinetics, and efficient accumulation efficiency. Morphological

studies such as high surface area, closely integrated interfaces, and small particle size are essential to develop effective electrochemical sensors for detecting phenolic compounds. By controlling the surface properties of nanocomposites, their applications can be expanded across various fields, from coating materials to electrochemical sensors for phenolic compounds. However, the realization of their full potential on a large scale necessitates a profound understanding of fundamental corrosion processes, microbial adhesion mechanisms, and additional studies to evaluate environmental risks and toxicity to marine environments caused by nanoparticles used in nanocomposites. Field tests in marine environments are also crucial for comprehending real conditions and developing effective coating materials against submerged marine organisms. Innovations such as self-healing coatings, environmentally friendly coatings, and intelligent coatings based on pH-controlled systems represent a new frontier in this field. Some recent advancements, as discussed in this review, have pointed to practical applications, particularly in anti-corrosion, antifouling, and electrode film coating materials. Ongoing research endeavors are expected to minimize economic and ecological losses associated with these issues.

## ACKNOWLEDGEMENTS

The authors acknowledge the funding support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canada First Research Excellence Fund. Khan N. thanks the scholarship provided by the School of Graduate Studies, Memorial University of Newfoundland.

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