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Graphene-based Coatings - A Corrosion Inhibiting Comrade

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Abstract

Corrosion has been an intense problem the industry has faced since the industrial revolution in the 18th century. As a result, the protection of the machine body from corrosion-causing environmental factors has been a crucial topic of interest of various researchers for many decades. To improve the machine's service life by inhibiting corrosion, graphene emerged as a revolutionary discovery. The main focus of this paper is concerned with anticorrosive coating derived from graphene and its derivatives. Graphene became evident as a revolutionary material because of its excellent properties. It has been observed that graphene coating has a more excellent corrosion inhibiting effect than a conventional coating. We have briefly discussed various manufacturing methods of graphene and graphene oxide. Industrial manufacturing of graphene is done by chemical vapor deposition. Recent studies reveal that graphene has turned out to be acceptable material for the preparation of polymer composites. Graphene-based polymer composite coatings have superior properties to regular graphene coatings and better corrosion inhibiting performance. These intriguing properties have inspired the research on hybrid graphene polymer composite materials.

Keywords: Graphene, Anticorrosive Coatings, Polymer Composite, Graphene Composite, Graphene Coating

Abbreviations

1. CVD: Chemical Vapor Deposition
 2. PMMA: Poly (methyl methacrylate)
 3. CP: Conductive Polymer
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1. Introduction

Corrosion is one of the most significant challenges faced by the metal industry. It is a naturally occurring method that converts a cultured metal right into a greater chemically strong shape inclusive of oxide hydroxide, carbonate, or sulfide. It is the sluggish destruction by aid of using chemical and/or electrochemical response with their environment. Environmental elements such as moisture, oxygen, and electrolyte are the main causes. Corrosion is hazardous to metallic materials' performance, reduces the service life of infrastructure and supply facilities, costs money, and puts occupational safety at risk. It has been a serious risk to the financial system and society for many years because it influences a number of the maximum broadly used substances when it comes to structural applications, one of the major problems withinside the coatings field. Many protective approaches have been proposed to prevent or suppress corrosion of metals, and among them, organic anti-corrosive coatings are one of the most effective techniques. Until recently, corrosion safety for metal changed into provided via way of means of zinc- and chromium-primarily based totally coatings; however, due to the negative effects of chromium on human fitness and the environment, its deliver and use in World are restricted. There is a growing demand for highly effective, environmentally pleasant and cheap products. Furthermore, revolutionary technology is transferring the focal point from safety in opposition to corrosion to its prevention in industrial production, most metals and alloys, such as copper (Cu), nickel (Ni), magnesium, and carbon steel, suffer from corrosion. Anti-corrosion coatings protect the underlying metal from corrosive media, reducing the risk of corrosion. Anti-corrosion coatings on metal surfaces can be covered for a cost-effective and effective anti-corrosion solution. Coatings having anti-corrosive properties ensure metal parts have the longest doable lifespan. Anti-corrosion graphene coatings have gained huge popularity in recent years. Research on graphene based anti-corrosion packages is presently targeted on natural graphene anti-corrosive coatings and graphene composite anti-corrosive coatings. These coatings might help to save space and money. A graphene coating has a better anti-corrosion effect than a conventional coating. Graphene, which is one atom thick, is the thinnest two-dimensional

carbonaceous material ever known. Since Geim and Novoselov followed a micro-mechanical stripping technique to put together single-layer graphene for the primary time, it has attracted great interest each from the medical in addition to the commercial community. Graphene is taken into consideration a structural monomer of carbon substances consisting of graphite, carbon nanotubes (CNTs), and fullerenes. With non-stop studies at the overall performance of graphene, numerous packages have been accomplished on graphene, such as optical components, gas cells, organic devices, and anti-corrosion coating of metals. These packages gain from graphene's extremely good overall performance attributed to its awesome houses, which include a strength of one hundred thirty GPa, a thermal conductivity of $5000 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$, a forbidden band width of virtually zero, a carrier mobility of $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, an excessive transparency of about 97.7%, a theoretically calculated precise surface area of $2630 \text{ m}^2 \text{ g}^{-1}$, a Young's modulus of 1100 GPa, and a breaking strength of a hundred twenty-five GPa, and those characteristic properties are equal to the ones of CNTs. Corrosion is one of the greatest challenges faced by the metal industry. It is a naturally occurring method that converts a cultured metal right into a greater chemically strong shape inclusive of oxide, hydroxide, carbonate or sulfide. It is the sluggish destruction of substances with the aid of using chemical and/or electrochemical response with their environment. Environmental elements such as moisture, oxygen, and electrolyte are the main causes. Corrosion is hazardous to metallic materials' performance, reduces the service life of infrastructure and supply facilities, costs money, and puts occupational safety at risk. It has been a serious risk to the financial system and society for many years because it influences a number of the maximum broadly used substances when it comes to structural applications, one of the major problems withinside the coatings field. Many protective approaches have been proposed to prevent or suppress corrosion of metals, and among them, organic anti-corrosive coatings are one of the most effective techniques. Until recently, corrosion safety for metal changed into provided via way of means of zinc- and chromium-primarily based totally coatings; however, due to the negative effects of chromium on human

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inclusive of oxide, hydroxide, carbonate or sulfide. It is the sluggish destruction of substances with the aid of using chemical and/or electrochemical response with their environment. Environmental elements such as moisture, oxygen, and electrolyte are the main causes. Corrosion is hazardous to metallic materials' performance, reduces the service life of infrastructure and supply facilities, costs money, and puts occupational safety at risk. It has been a serious risk to the financial system and society for many years because it influences a number of the maximum broadly used substances when it comes to structural applications, one of the major problems withinside the coatings field. Many protective approaches have been proposed to prevent or suppress corrosion of metals, and among them, organic anti-corrosive coatings are one of the most effective techniques. Until recently, corrosion safety for metal changed into provided via way of means of zinc- and chromium-primarily based totally coatings; however, due to the negative effects of chromium on human fitness and the environment, its deliver and use in World are restricted. There is a growing demand for highly effective, environmentally pleasant and cheap products. Furthermore, revolutionary technology are transferring the focal point from safety in opposition to corrosion to its prevention In industrial production, most metals and alloys, such as copper (Cu), nickel (Ni), magnesium, and carbon steel, suffer from corrosion. Anti-corrosion coatings protect the underlying metal from corrosive media, reducing the risk of corrosion. Anti-corrosion coatings on metal surfaces can be covered for a cost-effective and effective anti-corrosion solution. Coatings having anti-corrosive properties ensure metal parts have the longest doable lifespan. Anti-corrosion graphene coatings have gained huge popularity in recent years. Research on graphene based anti-corrosion packages is presently targeted on natural graphene anti-corrosive coatings and graphene composite anti-corrosive coatings. These coatings might help to save space and money. A graphene coating has a better anti-corrosion effect than a conventional coating. Graphene, which is one atom thick, is the most thinnest two-dimensional carbonaceous material ever known. Since Geim and Novoselov followed a micro-mechanical stripping technique to put together single layer graphene for the primary time, it has attracted great interest each from the medical in addition to the commercial community. Graphene is taken into

consideration a structural monomer of carbon substances consisting of graphite, carbon nanotubes (CNTs), and fullerenes. With non-stop studies at the overall performance of graphene, numerous packages has been accomplished on graphene, such as optical components, gas cells, organic devices, and anti-corrosion coating of metals. These packages gain from graphene's extremely good overall performance attributed to its awesome houses, which include a strength of one hundred thirty GPa, a thermal conductivity of $5000 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$, a forbidden band width of virtually zero, a carrier mobility of $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a excessive transparency of about 97.7%, a theoretically calculated precise surface area of $2630 \text{ m}^2 \text{ g}^{-1}$, a Young's modulus of 1100 GPa, and a breaking strength of a hundred twenty five GPa, and those characteristic properties are equal to the ones of CNTs. Corrosion is one of the significant challenges faced by the metal industry. It is a naturally occurring method that converts a cultured metal right into a chemically robust shape, including oxidation of the metal, hydroxide formation, carbonate, or sulfide formation. It is a slow process of degradation of substances that are caused due to chemical and/or electrochemical stimulus with their environment. Environmental elements such as moisture, oxygen, and electrolyte are the primary causes¹. Corrosion is hazardous to metallic materials' performance, reduces the service life of infrastructure and supply facilities, costs money, and puts occupational safety at risk. It has served as a severe risk to the financial system and society for many years because it influences a number of the maximum broadly used substances for structural applications, one of the severe complications withinside the coatings field. Numerous protective approaches have been proposed to prevent or suppress corrosion of metals, and among them², organic anti-corrosive coatings are one of the most effective techniques². Recently corrosion safety for metal changed using zinc and chromium-primarily based coatings; however, due to the adverse effects of chromium on human fitness and the environment, its delivery and usage are restricted. There is a growing demand for highly effective, environmentally pleasant, and cheap products. Furthermore, revolutionary technologies transfer from safety in opposition to corrosion to prevention in industrial production. Metals and alloys, like copper (Cu), nickel (Ni), magnesium, and carbon steel, have to undergo corrosion³. Corrosion inhibiting coatings protect the metal from corrosive agents, thus minimizing corrosion. Anti-corrosion

coatings on metal surfaces can be covered for a cost-effective and practical anti-corrosion solution. Coatings having anti-corrosive properties ensure metal parts have the most extended doable lifespan. Anti-corrosion graphene coatings have gained massive popularity in recent years. Research on graphene-based corrosion inhibiting packages is being presently targeted on natural graphene corrosion inhibiting coatings and graphene composite non-corrosive coatings. These coatings might help to save space and money. A graphene coating has a better corrosion inhibiting effect than a conventional coating.

Graphene, one atom thick⁴, has been the thinnest two-dimensional carbonaceous material ever known⁴. In the beginning, as Geim and Novoselov had followed the micro-mechanical stripping technique by putting together graphene with a single layer, it captivated the interest of the commercial community⁵. Graphene is considered the structural monomer is existing in carbon substances consisting of graphite, carbon-nanotubes (CNTs), and fullerenes⁶. Along with extensive studies on the overall performance of graphene, numerous packages have been accomplished, such as optical instruments, gas cells, organic devices, and corrosion inhibiting coating of metals. These packages result from the excellent performance of graphene attributed to its characteristics, equivalent to those of CNTs.

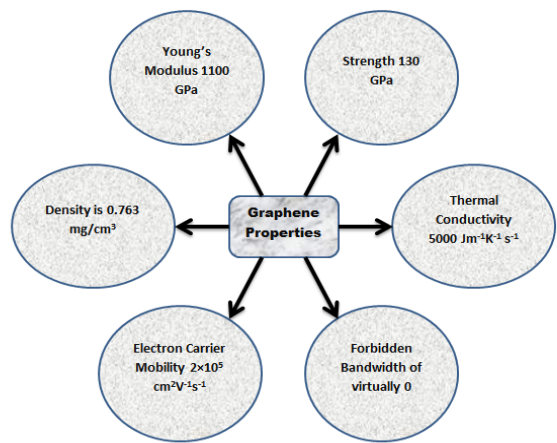


Fig 1 – Properties of Graphene

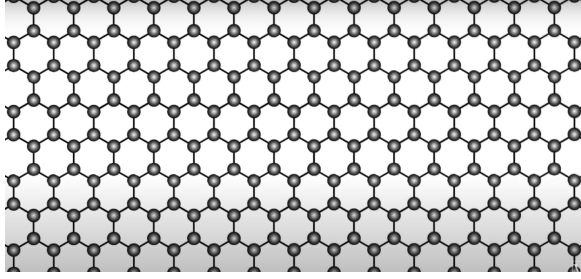


Fig 2 – Structure of Graphene

2. Gravity of Corrosion

The corrosion procedure is sluggish and takes place at surfaces of metals; however, the losses incurred because of corrosion are extensive waste and the destruction of machines, equipment, and distinctive styles of steel products. Corrosion losses cannot be calculated solely in metal prices; the high cost of fabrication into gear, devices, tools, and systems must also be considered. The severity of the problem can be determined by estimating the loss of metal due to corrosion to be between 2 and 2.5 billion dollars per year globally. If the outcomes arising due to corrosion are to be minimized, the engineer needs to apprehend the corrosion mechanism. Moreover, he'll be more capable of preventing difficult corrosion situations and offer concurrent protection in opposition to corrosion.

3. Why Graphene?

Humanity has always been fascinated by the behavior of various mechanisms at the subatomic level. Deep knowledge and understanding of many newly discovered materials on a much smaller scale has recently become possible, enabling the development of instruments to peer into the world of atoms and molecules. The change in the properties of the materials when combined has become more evident in many respects. This accumulation of molecular order gave birth to one of the materials named graphene, with the most significant potential of the century. The properties of graphene are derived from the complexity of its chemical configuration, making them suitable for a wide variety of commercial and primary uses. Graphene has shown very complex compositions, depending on the interactions with other chemicals, e.g., hydrogen. Various forms of graphene, such as monolayer graphene, graphane, and graphone, have different properties that set them apart from graphite. Novoselov studied monolayer

graphene, which was originally produced from graphite.

3.1 Thermal Properties

Thermal management is one of the most critical components in the reliable operation of electronic equipment that generates a significant quantity of heat during operation. Graphene is used as a heat sink in electrical circuits because of its excellent thermal conductivity[7]. Graphene is envisioned as a significant component in electronics due to covalent solid connections and phonon dispersion, leading to high thermal conductivity. At room temperature, the heat conductivity of pure single-layer graphene is substantially higher than other carbon allotropes, like carbon nanotubes, which have previously been documented⁴.

3.2 Optical Properties

Graphene is transparent; hence it has found use in various photonic devices that require conducting and thin transparent layers. The fine-structure constant of mono-layer graphene is $1/37$, and it absorbs 2.3 percent of white light (97.7% transmission). The stacking sequence and orientation influence the optical properties of graphene; thus, bilayer graphene exhibits new optical features. Graphene has a low resistance (106 cm) and excellent transparency, making it ideal for electrodes in liquid crystal devices. Graphene is such a kind of material that is light, strong, flexible, chemically stable, and inexpensive⁸.

3.3 Chemical Stability and Reactivity

Graphene's chemical stability is attributed to its honeycomb network, with strong in-plane sp^2 hybrid bonds[8]. Graphene's chemical inertness has prevented the oxidation of metals and metal alloys. Chen et al. (2011) were the first to demonstrate graphene's oxidation resistance when they used the CVD process to coat Cu and Cu/Ni with graphene. It is intended to improve the durability of prospective optoelectronic devices due to their chemical stability and inertness^{9,10}.

Graphene oxide dissolves in polar as well as in non-polar fluids. Since each graphene atom is on the surface, it can interact with any target gas or vapor species molecule. As a result, graphene shows a unique feature of chemical reactions. This characteristic allows you to change the conductivity

of graphene by choosing the suitable molecule to adsorb on the surface of carbon monomer 'graphene.' However, because of the two-dimensional structure of graphene, each atom is accessible for a chemical reaction from two sides. Furthermore, a carbon atom at the graphene sheet's edge has a unique chemical reactivity, and flaws inside the sheet also boost the chemical reactivity. The number of layers, the reactivity, and the electrical properties of graphene are dependent on the relative location of atoms in adjacent layers⁴.

3.4 The Intriguing Electronic Properties

A unique feature of graphene is that it can withstand highly high currents of electricity. The bonding in graphene helps with electron conduction and forms a slight contact amongst graphene layers. Description of charge carriers in graphene can be done using the "Dirac equation" rather than the "Schrödinger equation"⁵. Attributing to both analogous carbon sublattices in graphene's honeycomb structure, cone-like valence and conduction bands overlap at the Fermi level at the K and K₀ regions in the "Brillouin zone"⁵. Graphene has a two-dimensional semiconductor with a null forbidden energy gap; thus it displays a well-defined ambipolar effect of the electric field, quasiparticles, and a substantial mean free path. With concentrations as high as 10¹³ cm⁻², graphene conducts either electrons or holes. It has an electron carrier mobility of about 5x10⁵ cm²V⁻¹s⁻¹. Electrons flow smoothly across the flawless honeycomb structure of graphene, resulting in such tremendous mobility. The charge carriers in graphene are relativistic particles with a rest mass of zero and an effective speed of 10⁶ cm⁻¹s⁻¹. The fundamental difference between Dirac fermions and the Schrödinger equation is that in the former, electrons traveling through the honeycomb lattice lose their effective mass⁴, resulting in⁴ quasi-particles, whereas, in the latter, it is the opposite.⁴

4. Production Methods

With Geim and Novoselov's discovery of graphene in 2004, a new sector in materials technology has opened. The ability of graphene to operate as a physical barrier against corrosive species was initially demonstrated by its impermeability to gases. Furthermore, graphene's chemical impermeability^[11] to oxidative etching up to 400°C, as well as an ultra-portable coating that doesn't dramatically alter optical characteristics, has triggered scientists to

work on the corrosion inhibitive functioning of graphene^[11].

4.1 Production methods for high-quality crystalline graphene

Manual exfoliation of graphite by serial peelings with scotch tape was the first successful method for isolating graphene. This approach gives quality single-crystal graphene flakes with a thickness of one atom. On the other hand, its throughput is extremely low, and upscaling of this approach is irrational.

Among the first methods for the synthesis to emerge was epitaxial graphene, produced by graphitizing silicon carbide (SiC). When single-crystal SiC is heated in an ultrahigh inert atmosphere, the Si atoms sublime, and the leftover C atoms graphitize. This may occur on Si as well as C terminated faces. Later, a C-rich buffer film beneath the produced graphene is covalently connected to the surface, whereas in the second case, the interaction with the substrate is much less. With the introduction of this synthesis method, it was quickly determined that the graphene produced is of exceptional quality, with charge carrier mobilities of electrons of up to 27,000 cm²V⁻¹s⁻¹ for graphene produced upon the C-terminated substrate cited as early as 2006. The cost of the substrates and the size restrictions and micromachining challenges of the resulting material remain the primary drawbacks of graphene extraction from SiC.

Since the preliminary reports reveal the surface separation of carbon atoms inside the graphene domains and continuous films from the transition metals, chemical vapor deposition (CVD) was one of the most popular graphene manufacturing processes. Yu et al., for example, exposed Ni foil to a combination of CH₄, H₂, and Ar at 1000°C to create high-quality graphene films. Hydrocarbon gas breakdown was used to explain the process followed by carbon atom migration into the metal foil. Carbon segregation occurs after a controlled cooling of such substrate, resulting in graphene layers at the surface. It has also demonstrated that it is possible to move this graphene onto insulating substrates by first applying a supportive layer to the produced film, etching the metal, and then applying the graphene support clump to a target substrate.

Copper quickly became the preferred growing medium due to its low ability to be soluble in carbon and catalytic influence on hydrocarbon prototype breakdown, permitting continuous SLG (Single layer graphene) film formation. Chemical Vapor Deposition for graphene production on Cu is often carried out near metal's melting point. The

accomplishment of low-temperature (300–400°C) growth has been done with microwave plasma assisting in the breakdown of hydrocarbon precursors. Graphene domains larger than millimeters and huge single-crystal films can be possibly made using the CVD process, also graphene with electron charge carrier mobilities as large as $350,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and development at low and extreme atmospheric conditions.

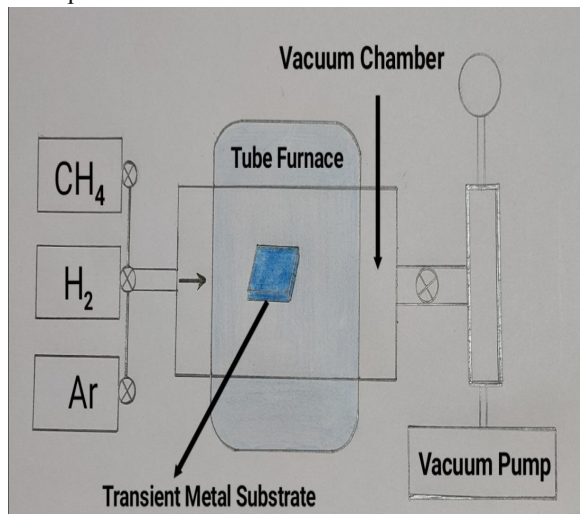


Fig 3 – Chemical Vapour Deposition (CVD)

H₂O molecules can also be fused between graphene and substrate, debilitating their bond and enabling the sample to be picked up with a stamp. In many situations, however, a supporting material must be utilized to prevent cutting off or degradation to the graphene film once it has been separated from the copper. PMMA is the most typical supportive material that is spin-coated on grown graphene at the start of the transfer process. Although, removing the PMMA support layer once the transfer is successful, which is usually done by immersing the transferred sample in acetone, leaves PMMA waste that is notoriously difficult to remove altogether. These residues affect graphene's characteristics, primarily through causing p-type doping. Various solutions to this difficulty have been published in the literature, such as high-temperature annealings and plasma treatments. Different approaches look for other supportive elements that may be eliminated without leaving behind residues instead of PMMA.

4.2 Manufacturing methods of graphene oxide (GO) and reduced graphene oxide (rGO)

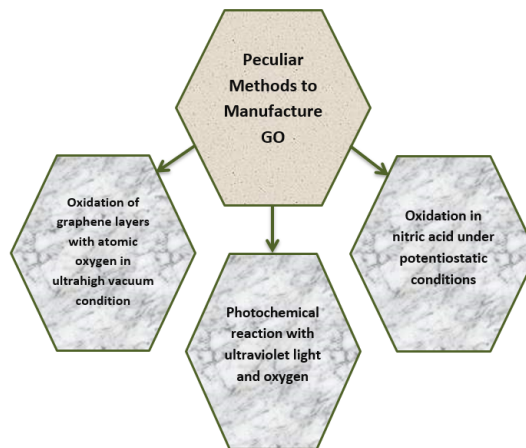


Fig 4 – Methods for Manufacturing Graphene Oxide (GO)

There are several ways to make GO; the most popular is oxidizing graphite and exfoliating it. A steady colloidal suspension of GO is created due to various chemical processes. Various scientists proposed different methods to prepare GO by oxidation of graphite.

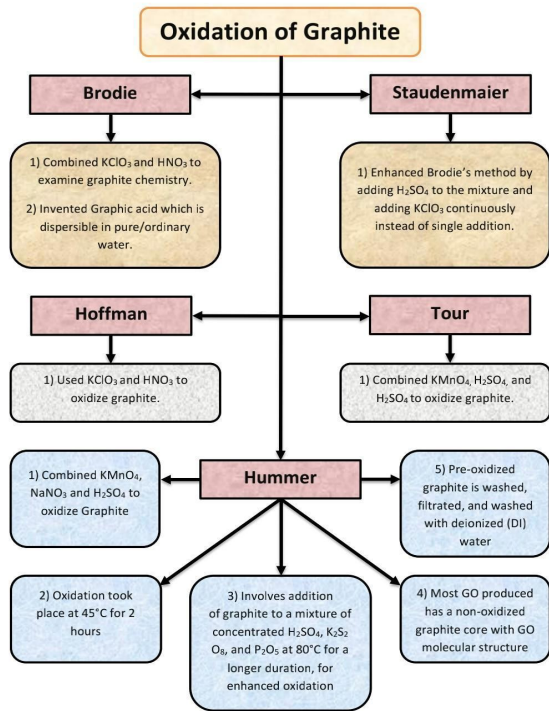


Fig 5 – Manufacturing of Graphene Oxide (GO) Don Various Scientists

Since then, various modifications based on the aforementioned synthetic methodologies have been applied.

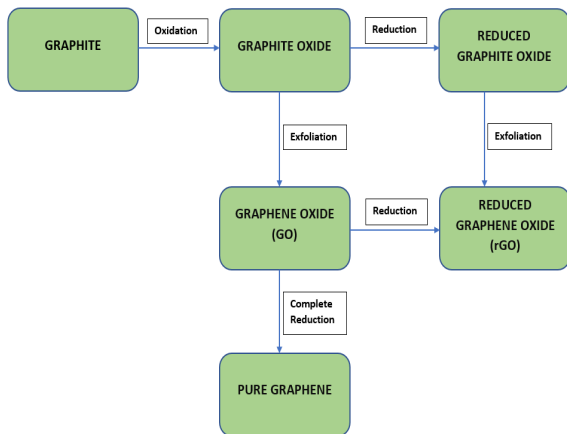


Fig 6 – General Methodology for Production of Pure Graphene

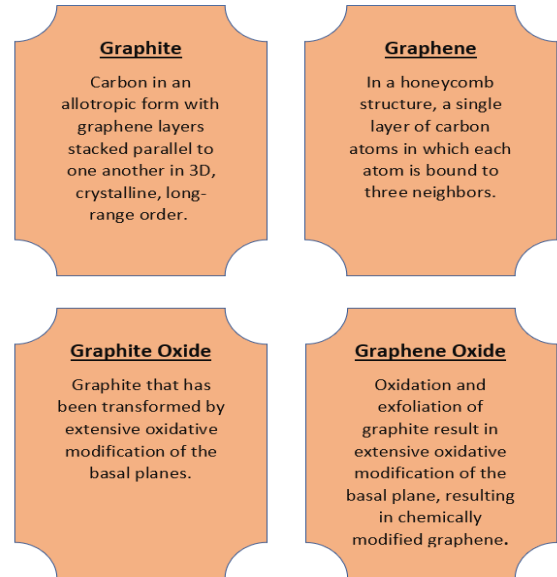


Fig 7 – Difference Between Graphite, Graphene and Their Respective Oxides

5. Graphene-based polymer composites

The yield and properties of such composites primarily depend upon the scale at which graphene materials are produced, as well as the homogeneous dispersion of graphene particles in polymer matrices^{12,13}. Both are crucial components in creating a composite with enhanced properties for various applications¹³. Graphene and its derivatives are becoming increasingly affordable and available in large quantities. Obtaining exfoliate individual graphene and its good yield remains a significant challenge. As a result, GO (Graphene oxide), rGO (Reduced graphene oxide), and frGO (Functional reduced graphene oxide) are commonly used¹².

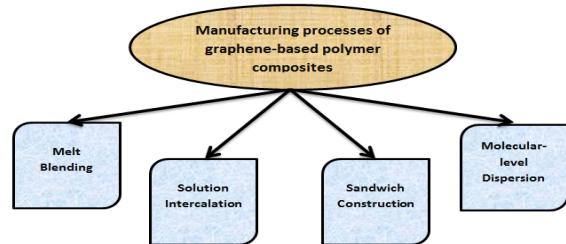


Fig 8 – Manufacturing Processes for Graphene-Polymer Composites

Graphene based polymer composites	Traditional Preparation Methods	Industrial Production Techniques
	<ol style="list-style-type: none"> 1) In situ polymerization 2) Solution blending/casting 3) Melt compounding 4) Combining the above production techniques appropriately 	<ol style="list-style-type: none"> 1) Exfoliation of graphite 2) Exfoliation/reduction of graphite oxide 3) Chemical Vapour Deposition [CVD]
	Characteristics on which the above Methods are based:	Factors on which the above Methods are based:
<ul style="list-style-type: none"> ❖ Molecular weight ❖ Polarity ❖ Hydrophobicity ❖ Reactive groups 	<ul style="list-style-type: none"> ❖ Time limit for achieving properties and form/morphology for intended graphene products ❖ Quality and implementations of graphene materials ❖ Scalability from lab to industry ❖ Stability and controllability of manufacturing 	

Table 1 – Graphene-Based Polymer Composites

6. Anti-corrosive Coatings

The anti-corrosion coating is responsible for creating a boundary between corrosion-causing agents and the metal surface, preventing the formation of corrosion-promoting chemicals on the surface. Failure of coatings may arise due to differences in metal structural properties and coating layer features, reducing their corrosion-fighting ability. Anti-corrosion coatings work by these two processes to resist corrosion:

[a] Barrier protection

[b] inhibitory effect.

By generating a thick coat, barrier protection cuts off the substrate from the corrosion-causing environment, thus avoiding corrosion: thickness, composition, and the existence of flaws all impact the barrier's effectiveness¹⁴. Corrosion inhibitors are metallic or nonmetallic compounds applied to a coating system to further protect against corrosion over the oxide layer's barrier protection².

Different multi-layered coatings with diverse characteristics and uses make up a corrosion-inhibiting coating system. Individual packages can either be metallic, organic, and inorganic, depending on the requirements of coating systems¹⁵. Traditional anti-corrosive treatment for severely corrosive marine environments often includes a primer, one or more intermediate coats, and a topcoat^{16,17}. The primer's job is to prevent corrosion on the substrate, thereby ensuring proper adherence¹⁶. As a result, primers for buildings in the marine environment or an atmospheric environment often have metallic zinc or inhibitive colors. The

intermediate coat aims to thicken the coating system and become impermeable to venomous species from accessing the material surface. The intermediate layer should also guarantee that the primer and topcoat adhere well. The upper coat is vulnerable to the elements and needs to provide the proper color and gloss to the surface. The upper coat needs to have a solid impedance to UV radiation and impedance to varying weather and impacts from objects. The coating's lifetime will be shortened due to environmental degradation caused by moisture, temperature, and harmful UV radiation. It's tough to judge a coating system's overall effectiveness and durability because it is influenced by various internal and external factors¹⁵. Formulators can regulate several aspects of the coating, including chemical, mechanical, and physical properties, along with chemical characteristics of the coating, by using binder systems, pigments, solvents, and additives^{14, 15}.

However, several of the displayed parameters, such as ambient qualities, are clearly beyond the control of the coating formulator. As a result, any assurance on a coating device's anti-corrosive efficacy and sturdiness has to be primarily based totally on "full-scale" (natural) blended with improved laboratory experiments. A coating device that's implemented to a metallic floor might also additionally include inhomogeneities which include air bubbles, cracks, microvoids, contaminants, trapped solvents, nonbonded and vulnerable areas, pigment-resins, and coating-substrate interfacial layers, further to the bodily and chemical residences of the coating and the substrate floor¹⁶. Each of those variables can affect the motion of competitive species throughout the coating and alongside the coating-substrate contact, and therefore at the degradation process¹⁶. Non-defective corrosion inhibiting coatings that usually guard the substrate with the aid of interfering the float of water, oxygen, and ions might also have lives of up to twenty years, demonstrating the significance of fending off defects in a coating. Coatings with bodily damage can have an extensively shorter lifespan. As a result, the permeability of anti-corrosive coatings to competitive species is essential to a coating device's capacity to buffer metals towards corrosion. Several structural residences of polymers on the permeability of natural coatings to oxygen and water had been addressed in the latest overview centered on the permeability of water and oxygen¹⁶. Internal tension in the coating, which occurs due to the coating's reluctance to

shrink, may increase the coating system's complexity. Internal stress in layers can substantially impact anti-corrosive coatings' endurance by causing adhesion loss, cracking, or cohesive failure¹⁸.

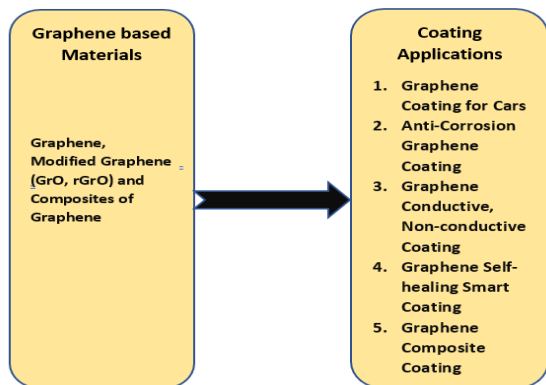


Fig 9 – Coating Applications of Graphene-Based Materials

6.1 Anti-Corrosive Graphene Composite Coatings

Graphene has an airtight balloon behavior and exceptional barrier nature against oxygen diffusion; hence it also provides oxidation resistance when applied as a coat on the substrate of metal. Graphene is a hydrophobic material owning its large surface area and a non-polar-based carbon structure, which contributes to its high impedance for reaction with oxygen and the inhibition of metal corrosion by opposing H-bonding with water. Scientist Kumar et al. studied the corrosion inhibiting properties of the fabricated composite. He deposited composite coatings of Nickel-graphene on a substrate of carbon steel. The corrosive resistance and the microhardness were found to be significantly improved. Despite having a large specific surface area and the fact that graphene has weak van der Waals interactions among layers, the function of graphene and its merits highly depend on its exfoliated state⁴, [19]. As a result, overcoming non-covalent interactions to produce graphene sheets free of basal plane defects is considered a critical problem in its application. An aqueous-based graphene exfoliation is a promising option for cost-effectiveness and environmental friendliness. Because of its hydrophobicity, dispersing graphene in water has been rarely studied and achieved.²⁰ Researchers have been using nonionic surfactants to disperse graphene in water for years, resulting in vastly concentrated exfoliation up to 1.5 percent by continuously adding nonionic surfactants to water.¹⁹ The dispersibility of graphene

in various polymer matrices has gotten a lot of attention recently, and its spawned applications in the field of nanocomposites of polymers.²⁰

6.2 Graphene/Polymer Nanocomposite Coatings

Micropores formed during curing by the volatilization of specific solvent and the gaps between polymeric chains are the two major flaws in the standard coating methods. These flaws make it easier for corrosive agents to quickly gain access to the metal substrate and make it harder for the standard coating structures to meet the requirements of long-lasting anti-corrosion. As a result, standard coatings are incapable of providing long-term anti-corrosion protection. Nanofillers, for example, mica, hydrotalcite, glass, montmorillonite, or silica to composites, helps improve the barrier performance of various coatings.

Though pure graphene corrosion inhibiting coatings offer excellent anti-corrosive properties, they have a lot of drawbacks in commercial applications. Also, metal corrosion is increased when the pure graphene coating is destroyed. Furthermore, pure graphene coatings have a high manufacturing cost, and significant commercial production is problematic.

Coatings that were organically made from polymers showed the capability of eradicating corrosion by creating a barrier between the metal surface and external corrosion-causing factors.^[2] Nevertheless, coatings made from polymers have been reported to be permeable to corrosion causing elements like water, chlorine, oxygen, boosting the corrosion initiation process while also reducing the polymeric coating's service time. Incorporating inorganic nanofillers inside the polymeric coating formulation, which have a fine grain size and large boundary volume, solves the problem of permeability and extends the coating's life.

So, most researchers are concentrating their efforts on developing corrosion inhibiting graphene-composite coatings. Anti-corrosive graphene-composite coatings outperform pure graphene coating. The strong chemical resilience and very high conductivity of graphene, also its excellent performance because graphene has unique and dynamic capabilities like self-healing^{21,22} improved mechanical characteristics²³, weather resistance²³, and the capacity of self-cleaning²³. All of these will result in the comprehensive performance of graphene-based composite coatings. Therefore, anti-corrosive graphene-composites coatings will bring a revolution in the corrosion-inhibiting coating field.

Comparison of coatings made up from polymer or those made up from graphene, the coatings providing corrosion protection for a short period have to face the mentioned dispersibility issue. Graphene/polymer composites provide an innovative physical barrier by minimizing the pores in the metal and the coating and dodging the path of diffusion followed by the corrosive media.

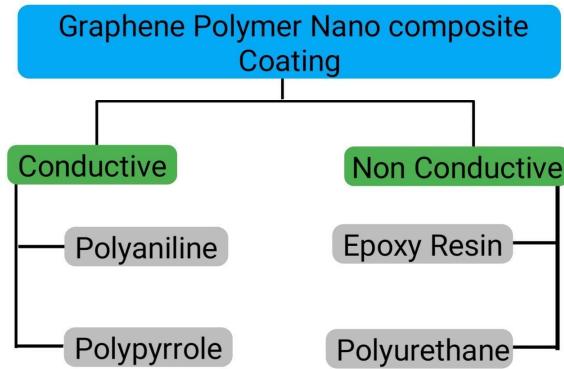


Fig 10. Types of Graphene Polymer Nano Composite Coating

6.3 Conductive Graphene Polymer Nanocomposite Coating

CP coatings have shown promise in improving the corrosion inhibiting properties of metal substrates in the past few years because they are non-toxic, eco-friendly, environmentally stable, and intend to bind strongly to the metal surface.¹⁹ With the suitable dopant molecules, conducting polymers could be directly electropolymerized onto the surface of metal substrates, resulting in a conductive and electroactive film with redox reactions with the metal substrate.¹⁹ The conductivity of conducting polymers is dependent on redox reactions, which include introducing and releasing dopant ions, which provide an excellent corrosion inhibiting mechanism.¹⁹ A physical barrier layer, switching of the electrochemical interface, anodic protection, facilitation of a protective oxide, forming of a modified CP metal interface, ennobling, and the use of dopant produced from the CP to provide more corrosion resistant surface layer have all been proposed so far for describing CP corrosion control with a wide variety of CPs and dopants.¹⁹

	Name of Coating	Properties	Applications
Conductive Graphene Polymer Nano composite Coating	1] Polyaniline Based Coatings [PANI]	<ul style="list-style-type: none"> a) Excellent air and thermal stability b) Ability to inhibit rusting c) Extraordinary physical barrier abilities d) Promoting remarkable graphite dispersion inside the polymer matrix 	<ul style="list-style-type: none"> ❖ Electrochemical systems for energy storage and conversion ❖ Electronic devices ❖ Electromagnetic and microwave shielding materials ❖ Sensors and biosensors
	2] Polypyrrole Based Coatings [PPy]	<ul style="list-style-type: none"> a) Excellent environmental stability b) Excellent electrical properties c) Convenience of fabrication d) Provide excellent protection on active metals e) Represent the highest impedance modulus f) Lowest corrosion current density g) Simple and less expensive film fabrication than PANI 	<ul style="list-style-type: none"> ❖ Widely used in corrosion-resistant materials ❖ Naval architecture ❖ Ocean engineering ❖ High Performance Super capacitor ❖ Preparation of Phosphate Coatings ❖ Non-Contact Heating Applications ❖ Flexible Electromagnetic Radiation Shielding ❖ Used for Strain Sensing

Table 2. Conductive Graphene Polymer Nano Composite Coating

	Name of Coating	Properties	Applications
Non Conductive Graphene Polymer Nano composite Coatings	1] Epoxy Resin Coating	<ul style="list-style-type: none"> a) Great tensile strength and modulus b) Superb chemical and corrosion resistance c) Significant adhesion and Dimensional stability d) Superior barrier performance against H₂O molecules e) Suppresses metal oxidation by oxygen reduction and metal salt solution f) Enhanced wear resistance performance g) Low shrinkage in cure h) Increased in electrical, thermal conductivity i) Protects polymer from atomic oxygen (AO) erosion 	<ul style="list-style-type: none"> ❖ Utilized as adhesives ❖ Used in: <ol style="list-style-type: none"> 1) Anti-corrosive Coatings 2) Flame Retardant Coatings 3) Thermal Conductive Coatings 4) High strength Coatings ❖ Used in structural materials ❖ Used in composite matrices ❖ Used in components on: <ol style="list-style-type: none"> 1) Aircraft 2) Wind turbines 3) Bridges 4) Ships 5) Cars and 6) Sports equipment

Table 3. Non-Conductive Graphene Polymer Nano Composite Coating

	Name of Coating	Properties	Applications
Non Conductive Graphene Polymer Nanocomposite Coatings	2] Polyurethane Coating [PU]	a) Provides excellent physical barrier between the corrosive environment and the surface of the metal substrate	❖ Applied on the surface of metal substrates as anti-corrosive material
		b) Superb corrosion resistance	❖ A film forming agent for the preparation of coatings with:
		c) Good flexibility	1) Great mechanical properties
		d) Strong adhesion to substrates	2) Enhanced corrosion inhibition performance
		e) Feasibility of tailoring its properties	❖ Used as adhesives
		f) Enhancement in the dispersion and compatibility	❖ Used in suspension components
		g) High tensile strength	
		h) High glass transition temperature (T_g)	
		i) Low Resistivity	
		j) High coefficient of static and dynamic friction	

Table 4. Non-Conductive Graphene Polymer Nano Composite Coating

Conclusion

This review emphasizes the recent developments in the field of anti-corrosive coatings based on graphene and its production as well as applications. As the durability of metal is dependent on corrosion inhibitive properties of the coating, graphene serves to have the potential to satisfy this requirement because of its excellent physiochemical, mechanical, thermal, optical, and electrical properties. Pure graphene coatings, conductive and non-conductive graphene polymer composite coatings, and various coatings based on graphene have considerably benefited when concerned about broad areas of applications. The performance of the anti-corrosive coatings can be determined by the shielding effect, bonding strength, and self-healing capability. Graphene-based anti-corrosive coatings fulfill all of these requirements. Because of the impermeability of graphene, graphene-based anti-corrosive coatings have become the barrier between corrosive media and the surface.

Because of its magnificent electrical conductivity, enhancement of cathodic protection can be carried out using graphene composite coatings. However, high electrical conductivity tends to increase local and galvanic corrosion. Composite coatings of graphene in the form of paints are being widely studied and utilized to enhance the corrosion protection of the material. As graphene has self-healing properties, any damage to the material can be repaired at zero cost. Research in this flow can significantly enhance the anti-corrosive behavior of the coating on the metal substrate. Since the wettability of graphene is extremely low, liquid corrosive media have very low adsorption on the coating, resulting in much less absorption. As a result, graphene coatings have greatly enhanced anti-corrosive applications.

Though the research in graphene-based anti-corrosive coatings has been done significantly, work on cost-effective graphene-based coatings needs to be initiated. Also, there is a lot of scope for research in hybrid graphene composite materials. Researchers have recently focused their attention on graphene dispersion in various polymer matrices, which has generated applications in the field of polymer nanocomposites. These materials must be environment friendly with their applications providing better anti-corrosive performance.

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