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Application of graphene in metal corrosion protection

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Application of graphene in metal corrosion protection

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Abstract. Single-layer defect-free graphene has excellent shielding performance and can prevent corrosion factors such as oxygen and water molecules from reaching the surface of the metal matrix. Based on the great application potential of graphene in the field of metal corrosion protection, this paper systematically summarizes the graphene film protective coating, graphene/organic protective coating and graphene-conductive polymer/organic protective coating. The existing problems of graphene film and the uniform dispersion of graphene in organic coating are analyzed and introduced in detail, and the future development of graphene-based anti-corrosion coating is prospected.

1. Introduction

Corrosion is a slow chemical or electrochemical process, which refers to the natural phenomenon that metal materials interact with oxygen and water to cause self-failure and destruction [1]. Problems such as bridge collapse, shipwreck and factory equipment damage caused by metal corrosion have brought huge losses to people's daily life and production. According to a 2012 survey conducted by the American corrosion engineering association, the direct economic loss caused by metal corrosion is as high as 2.2 trillion dollars per year worldwide [2]. Although it is impossible to avoid the occurrence of metal corrosion, the mechanism of metal corrosion can be studied to find effective means to protect the metal so as to slow down the rate of metal corrosion and reduce the harm caused by corrosion. Common metal protection technologies include cathodic protection, corrosion inhibitor protection, metal coating and surface organic coating. The above three methods have the problems of high cost of use, pollution to environment and limited application environment. The surface organic coating method is the most commonly used and effective metal protection method, which is to cover the metal surface with an organic protective film to avoid direct contact between the metal and the corrosive medium in the environment, so as to reduce the chance of chemical or electrochemical reaction of the metal [3]. However, a considerable part of the traditional organic coating contains toxic heavy metals such as chromate, lead and zinc, which has certain safety risks and environmental pollution risks. It not only consumes a large amount of non-renewable energy, but also is extremely unfavorable for the sustainable development of society and economy [1]. It is worth noting that the more easily corrosive media such as water, oxygen and ions can reach the coating/metal interface, the more likely the metal corrosion will occur under the coating. Therefore, it is a hot spot in the field of metal corrosion protection to seek a metal surface coating with good shielding performance and environmental friendliness. In addition, electrochemical method is often used to evaluate corrosion resistance and failure detection of coating. Generally, the lower the corrosion current of the coating, or the higher the impedance at low frequency, the better the corrosion resistance of the coating.



Graphene is a two-dimensional material with a single laminated structure with a thickness of only one atom diameter (about 0.35 nm), which is expected to become a new generation of revolutionary material (figure 1) [4]. Single-layer defect-free graphene coating has excellent shielding performance [5], which can prevent corrosion factors such as oxygen and water molecules from reaching the surface of the metal matrix, and is considered to be the thinnest corrosion protection coating known [6]. In addition, graphene has unique and excellent thermal, electrical and mechanical properties (such as high strength, good tribology properties, etc.) [7], and will become the most ideal anti-corrosion coating. The development of graphene materials, including graphene-based anti-corrosion coating for marine engineering, is highlighted in the cutting-edge new material of the new material section of “made in China 2025”. Based on the great application potential of graphene in the field of metal corrosion protection, this paper reviews the research progress of graphene film protective coating, graphene/organic protective coating and graphene-conductive polymer/organic protective coating.

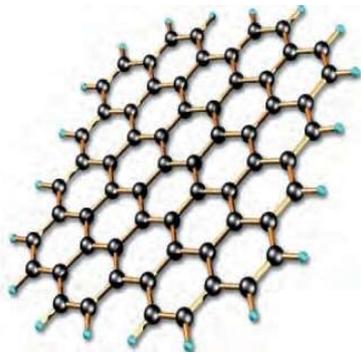


Figure 1. Structure of graphene

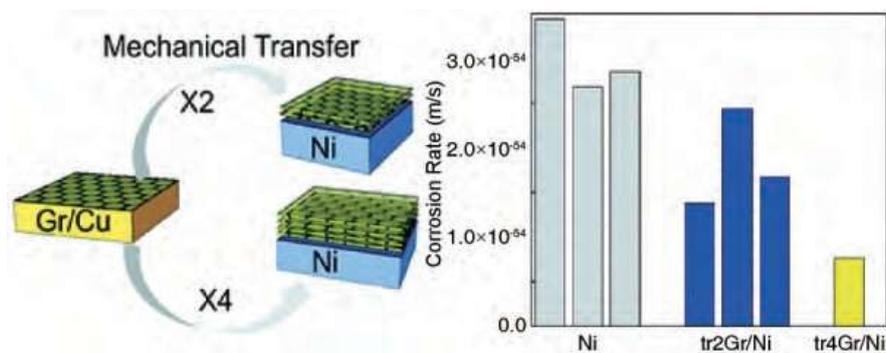
2. Graphene film protective coating

The preparation methods of graphene films [8-10] mainly include mechanical peeling, SiC epitaxial growth, chemical vapor deposition (CVD) and Redox process. Among them, the CVD method has the advantages of easy operation, high quality, large growth area and easy transfer of growing graphene [11], and the graphene film prepared by this method can be directly used for corrosion protection of metal (see table 1). In the process of preparing graphene sheet by CVD, the properties and materials of the matrix will affect the structure and properties of graphene to a certain extent. The strength of the bond between graphene and the metal is closely related to the distance from the metal to the carbon atomic surface. Graphene has different stable structures on different metal surfaces. Compared with gold, silver and palladium, copper, nickel and cobalt metals have much weaker interfacial force with carbon atoms. Therefore, these metals are the main growth matrix of graphene obtained by CVD [12].

Prasai et al. [13] successfully grew graphene films on the surface of copper by CVD method, and covered the surface of nickel with four layers of graphene by transfer method. Compared with bare nickel, the corrosion rate of nickel matrix coated with four layers of graphene decreased by four times in Na₂ SO₄ solution and the corrosion resistance increased greatly with the increase of the number of graphene coating on the surface (figure 2). The corrosion rate of graphene films grown on the surface of copper decreased by 7 times in the Na₂ SO₄ solution. They also studied the failure process of graphene coatings using electrochemical impedance spectroscopy (EIS). The results show that graphene films can play a physical shielding role between the metal matrix and the corrosive medium, which can greatly reduce the corrosion rate of the metal matrix, and have a strong protective ability for nickel and copper metals. In addition, although the graphene coating itself has not been damaged by the corrosive medium, the metal matrix in the cracks and defects of the graphene coating has been significantly corroded.

Table 1. Performance of graphene anticorrosion coatings

Substrates	Preparation method	The performance of garphene film	Ref
Cu and Ni	CVD	In an acerated Na ₂ SO ₄ solution: Direct coated copper films were 7 times slower than corroded bare copper. Direct coated nickel substrates were corroded 20 times slower than bare nickel.	13
Cu	CVD	Graphene films on the Cu substrate improved the corrosion performance of the material for a short period of time.	14
Cu	CVD	Graphene greatly eliminates the toxicity of Cu by inhibiting corrosion and reducing the concentration of Cu.	15
Ni / SUS304 stainless steel	CVD	Graphene-coated steel exhibits outstanding anti-corrosion properties.	16
Ag	CVD-Transfer	In 0. 1M NaCl solution: The corrosion rate of Ag is reduced by 66. 3 times with the use of graphene coating.	2
Cu	electrodeposition	In 3. 5% NaCl solution: The inhibition efficiency of graphene coated copper was calculated to be 94. 3% .	17
Cu	acetone-derived graphene	In 3. 5% NaCl solution: The corrosion inhibition efficiency of graphene coating on Cu surfaces was 97. 4% .	18

**Figure2.** Corrosion rates of bare Ni samples and the samples where graphene is transferred onto Ni substrate

Zhang et al. [15] used CVD method to grow graphene protective coatings adapted to biological growth on copper foil, preventing the corrosion of copper surface in different biological environments. The biological survival test showed that after 1 day of cell culture, the relative cell survival rate of bare copper was close to zero, while the cell survival rate of the copper matrix covered with graphene was 100%. This indicates that the graphene-coated copper foil can eliminate the toxicity of copper by inhibiting the corrosion of copper and reducing the production of Cu₂. In addition, the assembly of thiol derivatives on copper foil coated with graphene can effectively prevent corrosion factors from diffusing in the defects and cracks of graphene coating, greatly improving the corrosion resistance of graphene to copper matrix.

Pu et al. [16] used CVD method to grow graphene films on SUS304 stainless steel and nickel-plated stainless-steel Ni/SUS304 matrix. Scanning electron microscope (SEM) results showed that the graphene coating coverage on Ni/SUS304 matrix surface was 100%, while only a small amount of graphene was covered on SUS304 matrix surface. Nickel plating on SUS304 stainless steel can reduce the formation of metallic carbides and catalyze the production of graphene at high temperature, thus solving the problem of poor graphitization on SUS304 stainless steel matrix. The polarization curve after immersion in 3. 5% salt solution showed that SUS304 stainless steel metal with graphene coating showed excellent corrosion resistance, and its corrosion current was only about 1/50 of bare Ni /SUS304 stainless steel.

At present, the CVD method can only obtain high-quality graphene coating on metal matrix such as copper and nickel, but the mechanical transfer technology can make the graphene coating cover the

surface of any metal material. Silver films are widely used in optical studies, but silver is unstable in the air and is easily oxidized and corroded. Although common protective coatings can prevent the corrosion of silver, but also affect the optical properties of silver. Zhao et al. [2] grew single-layer graphene films on copper matrix by CVD method, and then transferred them to silver surface by mechanical transfer method as a transparent ultra-thin protective coating (figure 3). The corrosion rate of the silver films covered with graphene decreased by 66.3 times compared with that of bare silver. It is highly impenetrable and transparent to corrosive media such as oxygen and water molecules. Therefore, the single-layer graphene coating on the silver film not only retains its original optical properties, but also greatly improves its chemical stability and resistance to oxidation and corrosion under harsh conditions.

Many studies have shown that [14,19,20] graphene films prepared by CVD have excellent corrosion protection effect on copper and other metals in a short time, because graphene can prevent the penetration of corrosion factors such as oxygen and water molecules. However, graphene films grown by CVD method have many defects and grain boundaries. After long immersion, oxygen and water molecules will permeate through these defects to cause metal corrosion, and the conductive graphene coating will promote the electrochemical reaction at the interface to accelerate corrosion [21]. Therefore, to prolong the service life of graphene film in metal corrosion protection, less defective graphene coating or composite use with polymer resin is needed.

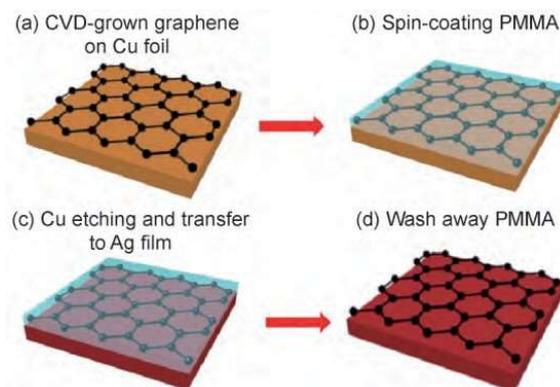


Figure 3. Schematic illustration of the process flow of graphene coating on a Ag thin film

3. Graphene/organic protective coating

The composite application of graphene and polymer resin can not only retain the excellent thermal, electrical and shielding properties of graphene, but also have the characteristics of strong adhesion and high mechanical properties of polymer resin. Therefore, the functional anticorrosive coating can be obtained after the two are used together. However, due to graphene's high surface area, strong Van der Waals force and π - π effect, it is easy to agglomerate, so the preparation of high-performance graphene/organic composite coating must first overcome the agglomeration of graphene and improve its dispersion in the polymer [22]. It has been reported in literature [23 ~ 26] that surface modification of graphene can improve its compatibility and dispersion with polymers. For example, Li et al. [23] used a titanate coupling agent to functionalize graphene, making it evenly dispersed in water borne polyurethane. When the graphene content is 0.4 wt%, the graphene lamella is arranged parallel to the metal base in the polyurethane, which can effectively prevent the infiltration of corrosion factors and achieve the best corrosion resistance.

Chang et al. [24] prepared graphene with different carboxyl content using heat reduced graphene oxide. Then they prepared PMMA/graphene (TRG) composite coating by photo-curing (figure 4). They studied the effects of the concentration of carboxyl in TRG on the anti-corrosion properties of PMMA/TRG coating. The results showed that the higher the concentration of carboxyl in TRG (33%), the better the corrosion resistance of the composite coating. This is because TRG with high carboxyl content is better dispersed in PMMA matrix, thus effectively improving the shielding effect on oxygen.

In addition, Chang et al. [25] also prepared PMMA/graphene composite coating (PGN) with bionic hydrophobic surface by Nano-casting technology. Its surface water contact angle was about 150° , anti-corrosion performance was increased by about 27 times than pure PMMA coating. PGN corrosion protection mechanism is shown in figure 5: ultra-hydrophobic surface is hydrophobic, thus reducing the absorption of water and other corrosive media on the coating surface and preventing the metal from being attacked by corrosive media. Carboxylation graphene disperses well in PMMA matrix, which improves the shielding effect on oxygen. Similarly, Chang et al. [26] obtained epoxy/graphene composite coating with hydrophobic surface (HEGC, FIG. 6) by using Nano-casting technology. Its surface water contact angle was about 120° , the anti-corrosion performance was increased by about 10 times than pure epoxy coating.

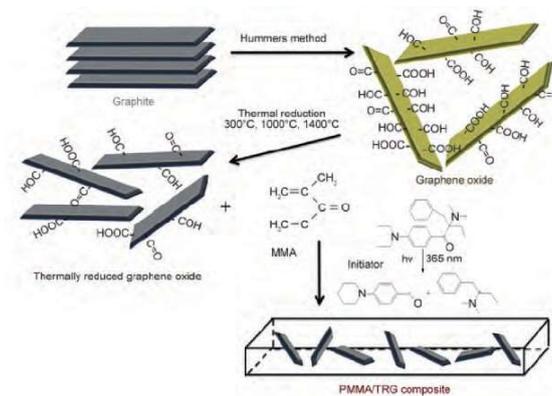


Figure 4. Preparation of PMMA / T R G composite coatings

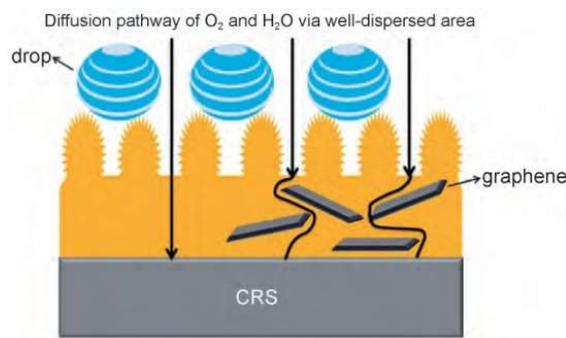


Figure 5. Schematic representation of the hydrophobic surface and oxygen following a tortuous path through PMMA and PGN materials

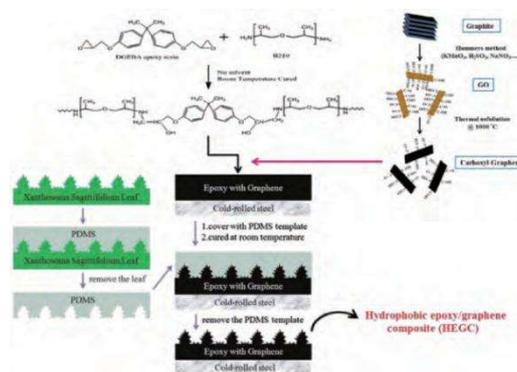


Figure 6. Preparation process for the hydrophobic surfaces of HEGC using the nanocasting technique

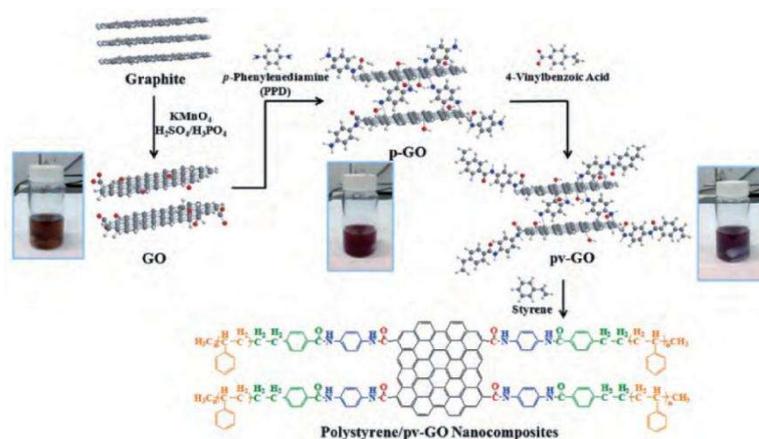


Figure 7. Preparation of PS / pv-GO nanocomposites



Figure 8. Preparation of PMMA-g-GO nanocomposites

The covalent or non-covalent bond functionalization of graphene by polymer can improve the compatibility and dispersion of graphene in the polymer and further improve the corrosion resistance of the polymer. Yu et al. [27] dispersed phenylenediamine / 4-vinylbenzoic acid modified graphene oxide (pv-GO) and styrene monomer in water and prepared polystyrene (PS)/pv-GO nanocomposites by in-situ microemulsion polymerization (figure 7). The corrosion resistance efficiency of PS/pv-GO composite coating with 2 wt% pv -GO was nearly 3 times higher than that of pure PS coating. Young's modulus increased from 1808.76 MPa to 2802.36 MPa. The initial decomposition temperature of coating increased from 298 °C to 372 °C. These improvements can be attributed to the complete separation of pv-GO dispersions, as well as greatly improved pv-GO/PS interfacial strength and shielding gas performance. Qi et al. [28] grafted PMMA on the surface of graphene oxide (GO) by surface initiation of atom transfer of radical polymerization, as shown in figure 8. This PMMA grafted GO (PMMA-g-GO) nanocomposite not only has the shielding property of GO, but also has the solubility of PMMA in various solvents, which makes PMMA-g-GO solvent processing and the coating thickness formed can be controlled. Electrochemical tests have shown that the PMMA-g-GO coating can effectively block the charge transfer at the copper-electrolyte interface, thus preventing the metal matrix from corroding in a strict environment. Zhang et al. [29] reduced GO in the presence of polyvinylpyrrolidone (PVP) to obtain PVP-rGO dispersion solution (figure 9). The PVP-rGO was added to the water-borne epoxy resin according to the content of 0 wt% ~ 0.7 wt%, and epoxy coating with different graphene content (GNS-epoxy coating, figure 9) was obtained. PVP non-covalent bond functionalized graphene can be uniformly dispersed in epoxy resin, effectively improving the adhesion and physical shielding performance of epoxy coating. Compared with the pure epoxy coating, the thermal decomposition temperature of the GNS- epoxy coating with PVP - rGO content of 0.7 wt % increased by about 73 °C. Young's modulus increased by about 213%, plasticity index decreased by 26.9% and corrosion rate decreased by about 4 times.

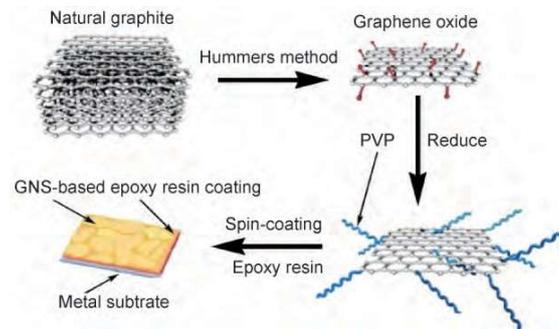


Figure 9. Synthesis process of GNS-epoxy coatings

Although graphene has excellent corrosion factor shielding performance, the high conductivity of graphene at the defects of coating greatly promotes the electrochemical corrosion of metals. Therefore, how to restrain the corrosion promotion effect of graphene and reduce the connection between graphene in the coating is another key problem for obtaining high anti-corrosion graphene coating. Sun et al. [30] inhibited the corrosion promotion activity of graphene through the graphene encapsulation technology. They used (3-aminopropyl) - triethoxysilane (APTES) to encapsulate graphene oxide, and obtained rGO/APTES composite material with a high aspect ratio lamella (figure 10), which was mixed with polyvinyl butyral (PVB) resin to improve the coating's shielding performance against corrosion factors, thereby impeding metal corrosion. Once the coating is scratched, APTES nanoparticles can act as an isolation layer, preventing the connection between graphene-metal/graphene and cutting off the electron transfer channel of electrochemical corrosion between graphene-metal, thus fundamentally inhibiting the corrosion promotion activity of graphene (figure 10). Compared with pure polyvinyl butyral coating, the corrosion rate of polyvinyl butyral coating with 5 wt% rGO/APTES decreased by about 65 times.

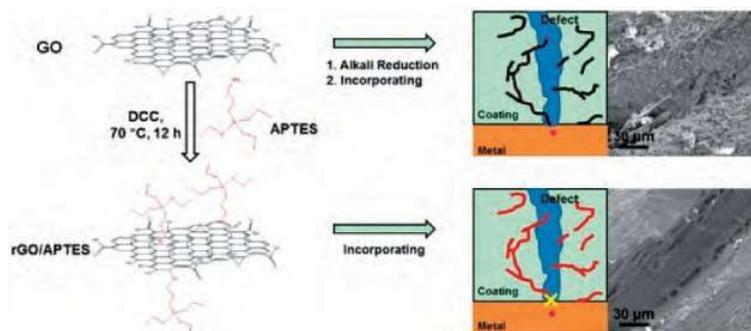


Figure 10. Preparation of rGO/APTES composites and SEM images of scratched copper coated by rGO/APTES/PVB and rGO/PVB

4. Graphene-conductive polymer/organic protective coating

Conductive polymers such as polyaniline show reversible Redox characteristics and metal corrosion resistance, and have become a new generation of environment-friendly anticorrosive materials [1]. Graphene has a high length-diameter ratio (about 500) and excellent corrosion factor shielding performance. Therefore, the composite of graphene and conductive polymer can further improve the corrosion protection of conductive polymer against metal. Chang et al. [31] prepared polyaniline/graphene composite (PAGCs) by in-situ polymerization (FIG. 11), whose shielding performance against water and oxygen and corrosion protection against metals were superior to polyaniline and polyaniline/clay composite (PACCs). This will be attributed to the higher length-diameter ratio of 4-aminobenzoic acid modified graphene (ABF-G) lamella material than non-conductive organic clay. Moreover, the grafted ABF-G can be dispersed well in polyaniline matrix, thus

extending the path of corrosion factors into the surface of metal base and improving the corrosion resistance of the coating. The results showed that PAGCs coating containing 0.5 wt% ABF-G had the best anti-corrosion effect, the oxygen and water molecular penetration rate decreased by about 86% and 88% respectively compared with the pure polyaniline coating, and the corrosion rate decreased by about 10 times. Sun et al. [32] prepared sheet graphene/oxidized polyaniline composite (GPCs) by in-situ polymerization-reduction/dedoping method, and its electrical conductivity was as low as 2.3×10^{-7} S/cm. The GPCs-PVB composite coating was prepared by adding GPCs to PVB resin. It can maintain high corrosion protection performance for a long time. This is because GPCs have a high length-diameter ratio and are evenly dispersed in the PVB matrix, which increases the path of the corrosive medium to the surface of the metal base. The corrosion rate of GPCs-PVB coating decreased by about 120 times, and the coating resistance increased by 105 times after being soaked for 140 hours, compared to the PVB coating with reduced graphene oxide only (rGO - PVBc).

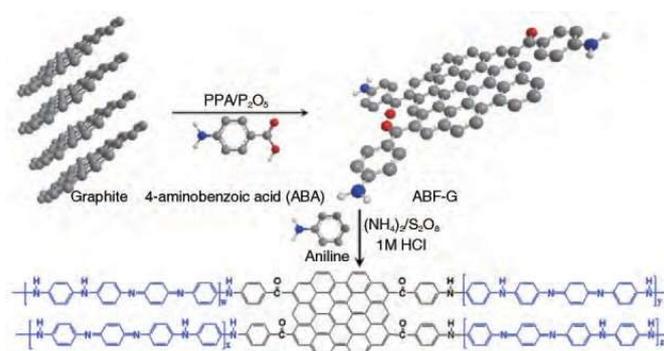


Figure 11. Preparation of PANI / graphene composites

5. Conclusion and outlook

After more than ten years of development, graphene has gradually become the "star material" widely concerned by the whole society, and its huge industrial development prospects have attracted worldwide attention. Graphene has excellent shielding properties and high length-diameter ratio and can be used in various forms in the field of metal protection. The application of graphene films, graphene/organic protective coatings and graphene-conductive polymer/organic protective coatings in the field of metal corrosion protection are reviewed. Graphene can act as an isolation layer between the medium and the base through the "maze" physical barrier to delay the corrosion rate of metal, greatly improving the corrosion resistance of metal. In addition, the conductive polymer modified graphene can effectively avoid the phenomenon of accelerated metal corrosion caused by electrochemical reaction in long-term immersion. However, the research and application of graphene in the field of metal corrosion prevention is still in its infancy and still faces great challenges. How to prepare graphene films with less defects and how to make graphene evenly dispersed or orientated in polymer resin by means of non-covalent bond are still to be solved. Therefore, in the future, there will still be a lot of in-depth research on graphene. I believe that in the near future, graphene will make greater progress in the field of metal protection.

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