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Review

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A comprehensive review on graphene-based anti-corrosive coatings

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Abstract

Graphene has attracted significant attention for applications in many industrial fields due to its excellent anti-corrosion properties, and a series of satisfactory results have been achieved. In recent years, the scope of research into graphene-based anti-corrosive applications has been extremely diversified and encompasses two aspects: pure graphene coatings and graphene composite coatings. In this study, the application of graphene coatings to metal anti-corrosion is comprehensively reviewed. First, the preparation methods for graphene and pure graphene coatings are described in detail. Second, the corrosion resistance, existing problems, and optimizations of pure graphene coating are presented. Third, methods for improving the dispersibility of graphene, such as chemical modification and surface decoration nanoparticles, are introduced. Next, the corrosion resistance, anti-corrosion mechanism, existing problems, and optimization measures of graphene composite coatings are summarized. Finally, future development directions for graphene anti-corrosive coatings are proposed, and their viability in near-future applications is discussed.

Keywords: Graphene; Anti-corrosion; Pure graphene coating; Graphene composite coating; Anti-corrosion mechanism; Problems and optimization

1. Introduction

Most metals and their alloys, such as copper (Cu), nickel (Ni), magnesium, and carbon steel, often suffer from corrosion in industrial production. Anti-corrosion coatings can isolate the underlying metal from the corrosive media, thus reducing the risk of corrosion. Covering

metal surfaces with anti-corrosion coatings is an effective and economical anti-corrosion method. In recent years, graphene anti-corrosion coatings have emerged extensively to protect metals from oxidation and corrosion. These coatings can decrease the volume and quantity of the coating. The anti-corrosion effect of a graphene coating is superior to that of traditional anti-corrosion coatings, without changing the original thermal/electric conductivity of the substrate [1,2].

Graphene is the thinnest two-dimensional (2D) carbon material. Since Geim and Novoselov adopted a micro-mechanical stripping method to prepare single-layer graphene for the first time, it has attracted significant attention both from the scientific as well as the industrial community [3]. Graphene is considered a structural monomer of carbon materials such as graphite, carbon nanotubes (CNTs), and fullerenes [4]. With continuous research on the performance of graphene, several applications has been carried out on graphene, such as optical components [5–7], fuel cells [8,9], biological devices [10,11], and anti-corrosion coating of metals. These applications benefit from graphene's excellent performance attributed to its outstanding properties, including a strength of 130 GPa, a thermal conductivity of $5000 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$, a forbidden band width of almost zero, a carrier mobility of $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a high transparency of approximately 97.7%, a theoretically calculated specific surface area of $2630 \text{ m}^2 \text{ g}^{-1}$, a Young's modulus of 1100 GPa, and a breaking strength of 125 GPa, and these properties are equivalent to those of CNTs [12–16].

Research on graphene-based anti-corrosion applications is currently focused on pure graphene anti-corrosive coatings and graphene composite anti-corrosive coatings. Excellent electrical conductivity, high surface area, and other outstanding properties of graphene play an important role in its anti-corrosion mechanism [17–24]. In this study, progress in the application of graphene in anti-corrosion coatings is deeply reviewed from four aspects. The second part describes pure graphene coatings. The preparation method and the corrosion resistance of the pure graphene coating are presented. Based on the problem that a pure graphene coating cannot provide the long-term protection of metals, optimization measures are proposed. The third part mainly includes the related content of graphene composite coatings. Methods involving both chemical modification and nanoparticles (NPs) decorated on a graphene surface are introduced to improve the dispersibility and compatibility of graphene in a coating matrix. Then, the corrosion resistance and anti-corrosion mechanisms of graphene composite coatings are introduced. Next, optimization measures are proposed based on the problems of graphene composite coatings. Finally, the fourth part introduces the future development direction of graphene anti-corrosive coatings.

2. Pure graphene coatings

2.1. Preparation of graphene

To improve the wide range of graphene applications in various fields, an appropriate selection of a source of graphene to obtain an optimal yield must first be carefully considered. At present, the yield of graphene limits the wider application of graphene. The methods for preparing graphene mainly include the micromechanical stripping method, the silicon carbide (SiC) epitaxial growth method, the redox method, and the CVD method.

In 2004, Geim et al. from the University of Manchester in the United Kingdom obtained single-layer graphene by the micromechanical stripping method, i.e., by stripping graphite with a tape. A layer of graphite was directly peeled off using tape and then was repeatedly pasted on the tape. As a result, the graphite sheet became increasingly thinner. Then, the tape was attached to the substrate, and a single layer of graphene was transferred to the surface [3]. This preparation method was simple and produced high-quality graphene. However, small-area graphene was obtained, and it could not be produced in a large quantities. Therefore, high-quality graphene prepared by mechanical stripping is generally applied to the study of the intrinsic properties of graphene.

A redox method has been developed based on the preparation method by Hummers et al. [11,25]. In this method, graphite is oxidized using potassium permanganate, concentrated sulfuric acid, and concentrated nitric acid to form graphene oxide (GO), and oxygen-containing functional groups are added between the graphite layers to increase the distance of the graphite layers. The dispersed GO sheets are obtained in solution by ultrasonic-assisted dispersion. The GO is then deoxygenated to graphene by strong reducing agents, such as hydrazine hydrate and sodium borohydride. This simple, low-cost method has been used for the large-scale preparation of graphene and has become an effective way to prepare graphene. However, during the strong oxidation and reduction processes, the structure of graphene is damaged, resulting in more defects and the poor quality of graphene.

The CVD method is considered the most promising method for preparing high-quality, large-area graphene with the greatest potential for the industrial production of graphene films [26,27]. To date, square-level graphene films have been successfully prepared by this method [26]. The specific process of the CVD method involves the following steps: passing hydrocarbon gases through the surface of the metal substrate, such as Cu and Ni foils, and heating to dehydrogenate the hydrocarbon gas to form graphene on the substrate surface [28]. This method is similar to the metal catalytic epitaxial growth method and includes the

advantage of preparation at a lower temperature, thereby reducing the energy consumption during the preparation process.

2.2. Preparation of a pure graphene coating

There are few preparation methods for pure graphene anti-corrosive coatings currently covered in the literature, most of which are mainly based on CVD. Of course, there are other studies that mention coating methods [29,30], spray methods [31], and electrochemical reduction methods [32–35]. However, the pure graphene protective film obtained by these methods exhibits poor quality and low coverage.

The CVD method can be used to directly fabricate a pure graphene anti-corrosive coating on the surface of the Cu foil [28,36] and the Ni foil [36]. The CVD method is developing, and the growth substrate has been extended to more types of metals, such as Rh [37], Au [38], Ti [39], Pt [40], Pd [41], and Co [42]. However, there are additional commercial metals (Mg, Al, Fe) that need to be protected, and steel and other related alloys generally cannot withstand the high temperatures required in the CVD process [43,44]. Pu et al. found that only a small area of the graphene film could be deposited onto the surface of bare stainless steel by CVD, while a stainless steel surface coated with Ni could deposit a large area of the graphene film [45]. To increase the range of CVD-protected metals, a mechanical transfer method was utilized to transfer the pure graphene anti-corrosive coating onto the substrate of the target metal substrate, as shown in Fig. 1 [46]. The specific steps involved in the method are as follows: (1) deposition of a layer of polymethyl methacrylate (PMMA) resist onto the graphene surface to form a PMMA/graphene/Cu interlayer; (2) dissolution of the Cu foil using an etchant; (3) deposition of PMMA/graphene on the target metal surface followed by drying; and (4) dissolution of PMMA using acetone, which leads to a graphene cover on the target metal surface. The application range of the CVD method is extended by the mechanical migration method.

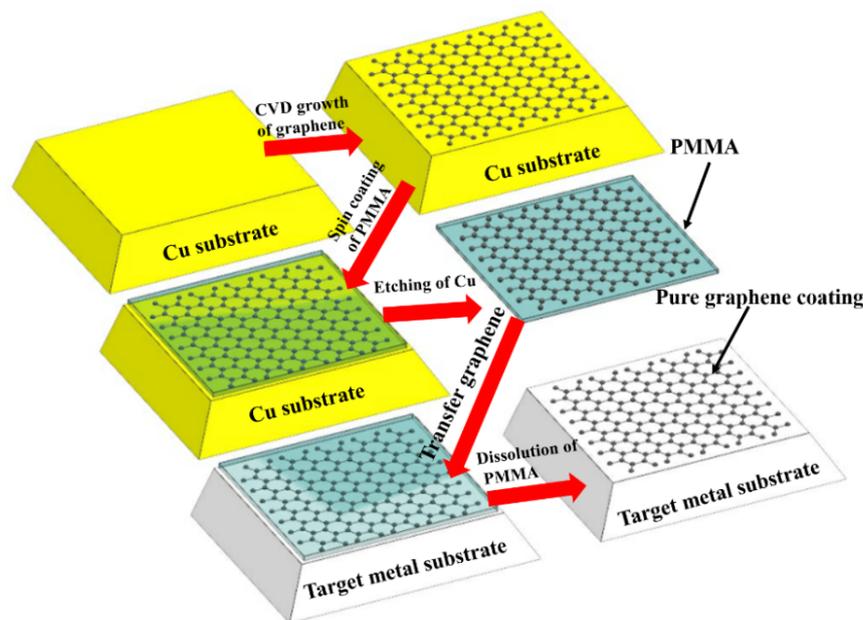


Fig. 1. Mechanical transfer method

However, after the mechanical transfer, the pure graphene anti-corrosive coating shows intrinsic contamination, which comes from the residue of the transferred polymer [26,47]. A pure graphene anti-corrosive coating prepared by CVD demonstrates high toughness. To prevent wrinkles and cracks, the transfer process requires a support layer such as PMMA [47], heat release tape, and polydimethylsiloxane (PDMS) [48]. These polymer residues are the sources of contamination for the graphene coating, which can affect the optical properties, heat transfer properties, and wettability of the pure graphene coating. When the surface of the pure graphene anti-corrosive coating is contaminated by hydrocarbons in air, the water contact angle increases, and the wettability deteriorates [49].

To reduce the pollutants on the surface and improve the anti-corrosion ability of the pure graphene anti-corrosion coating after mechanical transfer, various approaches have been employed, such as annealing [49,50], using a new polymer transfer method [51], and even a polymer-free transfer method [52,53]. These methods render the application of the pure graphene anti-corrosive coating prepared by the CVD method more widespread.

2.3. Anti-corrosion performance of the pure graphene coating

The corrosion resistance of pure graphene coatings for metals dates back to 2011. For the first time, Chen et al. used a pure graphene coating prepared by CVD to protect Cu and a Cu/Ni alloy from air oxidation. Chen and coworkers prepared a variety of samples, namely, a Cu foil covered with a pure graphene anti-corrosion coating, a Cu/Ni alloy foil covered with a pure graphene anti-corrosion coating, bare Cu, and a bare Cu/Ni alloy. These samples were

heated for 4 h in air at 200 °C and soaked in 30% H₂O₂ for 45 min. It was found that the apparent colour of the Cu foil and the Cu/Ni alloy foil covered with the pure graphene coating did not change before and after heating, while the unprotected sample showed a significant colour change and severe oxidation, as shown in Fig. 2(a) (b). The scanning electron microscopy (SEM) images showed that the Cu foil and the Cu/Ni alloy foil covered with the pure graphene coating were clearly visible before and after annealing, and a small amount of white Cu₂O corrosion product was produced on the coating defects. The surface of the bare sample (without the pure graphene coating) was very rough, and the image became blurred due to the charging effect caused by the accumulated charges on the surface of the insulated copper oxide, as shown in Fig. 2(c)(d) [54].

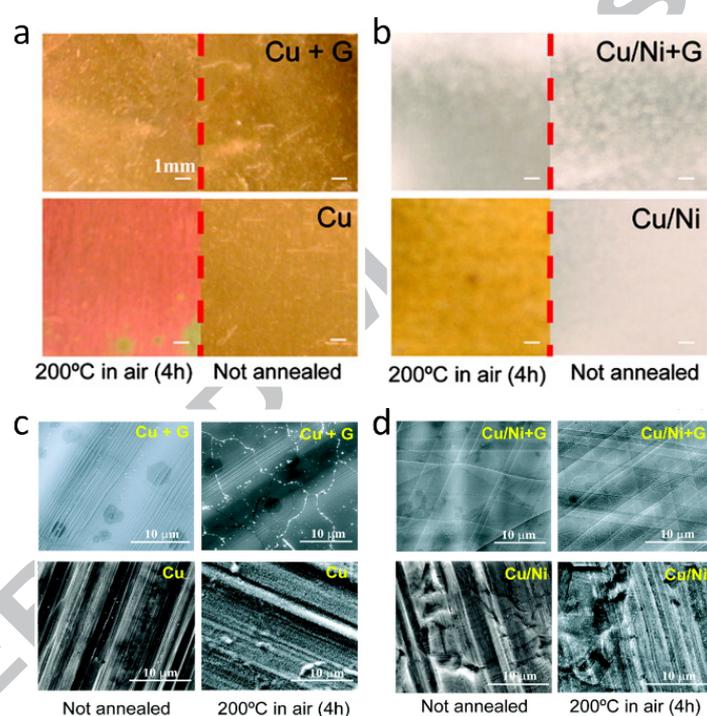


Fig. 2. Photographs of the Cu and Cu/Ni foils covered and not covered with pure graphene coating before (a) (on the right side of the red line) and after (b) (on the left side of the red line) annealing in air (200 °C, 4 h). SEM images of the Cu and Cu/Ni foils covered and not covered with pure graphene coatings before (c) and after (d) annealing in air [54]

Subsequently, Prasai et al. studied the ability of pure graphene anti-corrosive coatings to protect the Cu and Ni metals in an aerated Na₂SO₄ solution. Tafel analysis showed that the corrosion rate of Cu coated with pure graphene anti-corrosive coatings was seven times slower than that of bare Cu. The SEM images indicated that the bare Cu was uniformly corroded, and numerous white copper oxide corrosion products were present on the surface. The Cu protected by the pure graphene anti-corrosion coating was hardly corroded, and only a small amount of corrosion products occurred in the cracks of the pure graphene

coating, as shown in Fig. 3(a). The corrosion rate of Ni covered with the pure graphene coating was 20 times slower than that of bare Ni. At the same time, the corrosion resistance of the pure graphene coating obtained by the mechanical transfer method was also verified. The corrosion resistance of the transferred 2-layer and 4-layer pure graphene coatings was compared. The corrosion rate of Ni covered with four layers of transferred graphene was four times slower than that of bare Ni, and the thicker the pure graphene coating was, the lower the corrosion rate was, as shown in Fig. 3(b), (c) and (d). This finding indicates that the transferred graphene still hinders the contact of the corrosive media with the substrate, which provides protection to the underlying metal [2].

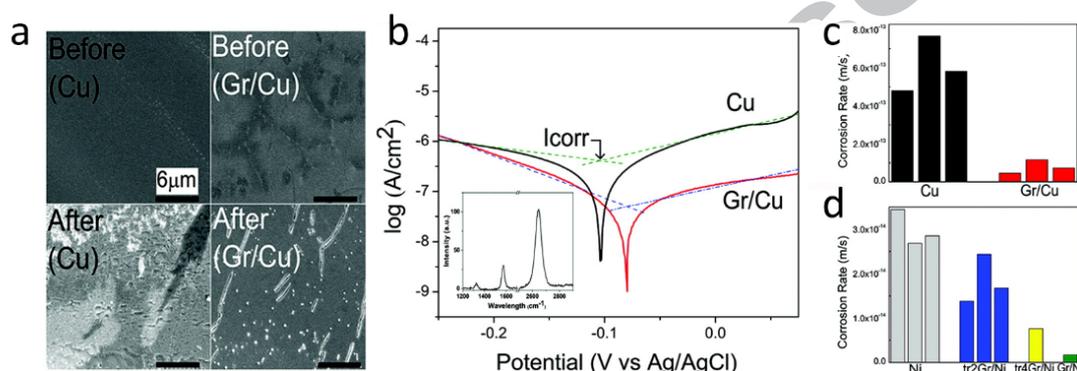


Fig. 3. (a) Comparison of the SEM images of Cu and graphene/Cu before and after corrosion, (b) Tafel curve fitting results, (c) Corrosion rates of the Cu and graphene/Cu samples extracted from the Tafel plots, and (d) Corrosion rate of the bare Ni sample and Ni substrate covered with graphene [2]

The pure graphene coating obtained by CVD not only provides protection for pure copper or pure nickel metals but also provides corrosion protection for substrates such as alloys, carbon steel, and stainless steel [55–63]. Zhang et al. demonstrated the migration of the graphene directly grown on the Cu foil to the surface of the NiTi alloy. Through electrochemical testing, the NiTi alloy covered with pure graphene coating exhibited a higher corrosion potential and less corrosion current than the bare NiTi alloy. These results proved that the pure graphene coating could enhance the corrosion resistance of the NiTi alloy. Moreover, the release rate of Ni ions in alloys coated with pure graphene was also reduced [60]. It is difficult to grow graphene directly on the surface of carbon steel. Ye et al. used laser induction to form a pure graphene coating on the surface of the carbon steel and verified its corrosion resistance. The corrosion resistance of carbon steel covered with the pure graphene anti-corrosion coating was comparable to that of stainless steel, even though the annual corrosion rate was lower than that of stainless steel (0.09 mm y⁻¹), which was only 0.05 mm y⁻¹ [61,62]. Zhu et al. developed a low-temperature CVD method using a solid carbon source (polystyrene (PS)) at 400°C to successfully grow a pure graphene coating on a

stainless steel substrate. Through electrochemical testing, it can be found that the corrosion rate of bare steel is $1.75 \times 10^{-13} \text{ (m} \cdot \text{s}^{-1}\text{)}$. The corrosion rate of the stainless steel specimen covered by the pure graphene coating is only $2.02 \times 10^{-14} \text{ (m} \cdot \text{s}^{-1}\text{)}$. The corrosion rates are reduced by a factor of 9 compared to that of bare steel. The sample was immersed in a NaCl solution for up to 30 days. The corrosion rate is still low, indicating that the pure graphene coating provides long-lasting protection for the metal, as shown in Fig. 4(d). After electrochemical testing, the bare steel was severely corroded, and the surface colour changed significantly. The surface of the sample protected by the pure graphene coating showed no significant change, as shown in Fig. 4(e)(f) [63].

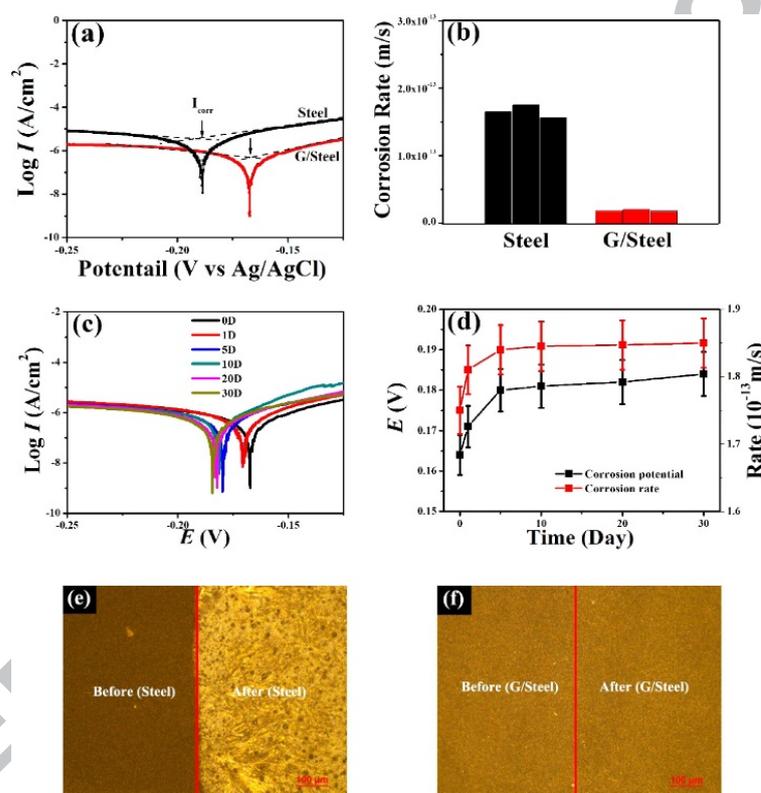


Fig. 4. (a) Tafel plots of steel and G/steel samples in a 5% sea salt solution. (b) Corrosion rates of the stainless steel and G/steel samples extracted from the Tafel plots. (c) The dependence of the current–voltage curve vs. time and (d) the corrosion potentials and corrosion rate as a function of the time in the G/steel sample. Optical images of (e) the pure stainless steel and (f) the G/steel substrate before and after electrochemical anticorrosion testing [63]

2.4. Problems associated with the pure graphene coating

Pure graphene can block the corrosive media from entering the anti-corrosion coating and can provide the long-term effective protection of the underlying metal substrate. However, some researchers have found some opposite phenomena. Dong immersed bare copper (U-Cu), annealed copper (A-Cu), and graphene-covered copper (G-Cu) in a NaCl

solution and evaluated the corrosion by electrochemical impedance spectroscopy (EIS). The corrosion rate of G-Cu during the first five days under soaking was lower than that of U-Cu. After five days, G-Cu was more severely corroded than U-Cu. Via the SEM imagery, the local corrosion of bare Cu was observed, while G-Cu was uniformly corroded. After annealing treatment, Cu exhibited the most serious corrosion. G-Cu offered good corrosion resistance for a short time. With increasing soaking time, the graphene coating peeled off, resulting in more serious corrosion than bare Cu [64]. Schriver studied the short-term and long-term performance of graphene-coated copper. In a short period of time (a few minutes or a few hours), the graphene coating provided effective protection in high temperature environments. For a longer duration, graphene led to the severe galvanic corrosion of Cu at ambient temperature, and even the corrosion resistance was not as good as that of bare Cu [65].

The factors resulting in the decline or even deterioration of the corrosion resistance of pure graphene coatings in the long term are discussed in detail. Prasai believed that corrosion occurred at the defects of graphene [2]. Heish considered that defects in the graphene grain boundaries led to the incomplete passivation of graphene. Defects in the graphene coating accelerated metal corrosion due to micro-galvanic corrosion. The defective area behaved similarly to a cathode that accelerates the corrosion [66]. Although a complete graphene layer could block gases and liquids and provide full protection to the metal substrate, the graphene defects may disrupt this protection by providing permeation pathways and even trapping chlorine atoms [67]. The surface of the single-layer graphene coating prepared by CVD generally has wrinkles, cracks, and defects, and it is found that the wrinkles are more susceptible to oxidation after high temperature annealing [68,69]. At the same time, graphene may suffer from external mechanical damage during the protection of metals, and these factors destroy the integrity of the graphene coating. Once the integrity of the graphene film is destroyed, corrosive media such as H_2O and O_2 pass through the defects, and the substrate metal is corroded. Moreover, the galvanic corrosion caused by graphene accelerates the destruction of the metal, as shown in Fig. 5 [70]. Furthermore, the expansion of the corrosion products on the metal surface causes the graphene coating to crack and peel off. Therefore, the bonding strength between the coating and the substrate is reduced, which causes more corrosive media to enter the gap between the coating and the metal to accelerate corrosion [71].

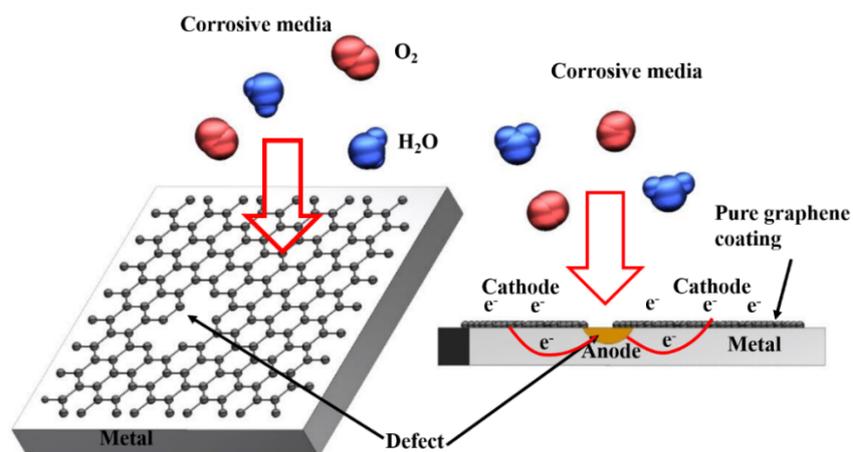


Fig. 5. Galvanic corrosion occurring in the defects of pure graphene coating

Another problem associated with the pure graphene coating is local oxidation, which is detrimental to the reliability and mechanical properties of the coatings [72]. Shi et al. [73] and Hui et al. [74] tested a single layer of graphene on Cu in accelerated oxidation media (hydrogen peroxide, H₂O₂). These investigators found the local oxidation of accumulated oxygen at defects and boundaries, which altered the structure of graphene by forming hillocks. The hillocks were first narrow, then became wider and were finally kept constant due to the propagation of the oxidation process. The Auger electron spectroscopy (AES) intensity proved that a high concentration of oxygen was produced on the coating surface after immersion. The nanoindentation test showed that the tips of the hillock structures have weaker bonds, and some of them ruptured during the oxidation process, which led to a decline in the mechanical strength or even the fracture mechanics. Lanza et al. further compared the oxidation phenomenon of graphene coated on Cu soaked in H₂O₂ (1 h, 4 h) and exposed to air (1 day, 29 days, and 113 days). During the oxidation process in H₂O₂ or air, the hillocks all formed at domain boundaries and both showed saturation-like behaviour. For graphene layers immersed in H₂O₂, the oxidation occurred in a controlled and progressive manner, while the oxidation that occurred in air was disordered [75].

2.5. Optimization of the pure graphene anti-corrosion coating

The single-layer pure graphene coating prepared by CVD encounters the above-mentioned problems, which limits the large-scale application of graphene as an anti-corrosion coating. Many researchers have adopted several optimization measures to obtain an improved graphene coating, which provides the long-term effective protection of metals.

First, a reasonable substrate is chosen or the binding at the interface is enhanced, as shown in Fig. 6. Weatherup et al. compared the long-term protection of graphene on Ni, Co,

Fe and Pt. These researchers found that a strong interaction between the graphene and metal is the key factor determining the long-term corrosion behaviour, and the formation of the passivating oxide could plug the defects and prevent the progression of the oxidation process [76]. Thus, researchers have been searching for a method to increase the interactions between graphene and the substrate. Kyhl et al. synthesized hydrogen-induced graphene on a Ir(111) surface; strong bonds were built at the graphene-substrate interface, which significantly improved the corrosion resistance against carbon monoxide [77].

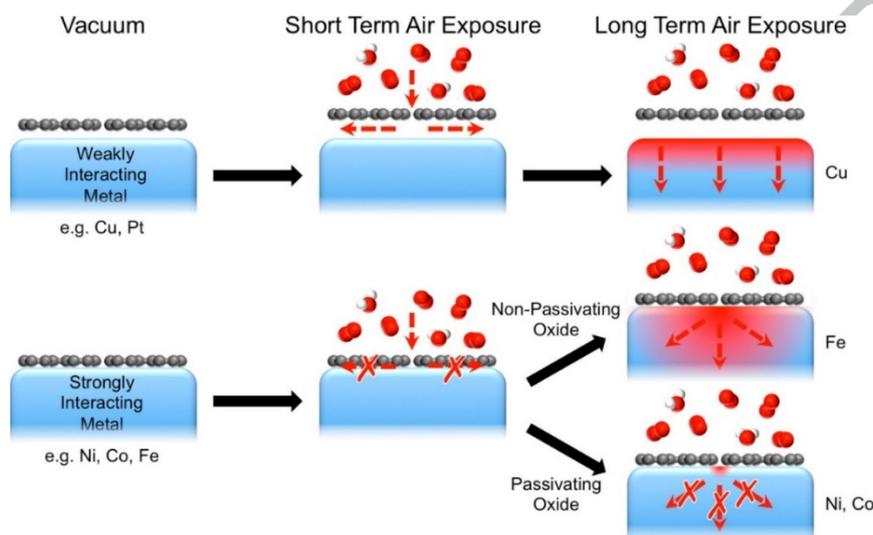


Fig.6. Passivation behaviour of different graphene-covered metals [76]

Second, CVD preparation parameters are optimized. Many variations in the preparation parameters affect the defect density of graphene and the durability of the corrosion resistance [78]. Through experiments, researchers have summarized a large number of preparation parameters, such as the H_2 volume flow [79–82], graphene growth temperature [1,79,81,83], cooling rate, and annealing time. Among these parameters, several key parameters have important implications for the quality of the graphene coatings prepared by CVD. Anisur et al. studied the effect of the cooling rate and hydrogen flow on the quality of the graphene coatings. When the cooling rate was slow, the preparation of the graphene coating was inhibited regardless of the presence or absence of the hydrogen flow. The wrinkles on the surface of the graphene coating without hydrogen flow decreased with an increase in the cooling rate, which provided a more durable corrosion resistance for the metal [78].

Third, multilayer graphene coatings are prepared. The preparation of multilayer graphene coatings is a simple and effective method to solve the defect problem [84] because the mutually matching defects overlap with each other and a spatial steric hindrance is formed, as shown in Fig. 7 [65]. However, different numbers of graphene layers affect the conductivity of the graphene coating, which leads to a change in the cathode

reaction rate [1]. Tiwari et al. deposited a multilayer graphene coating on the surface of Cu. Electrochemical tests revealed that the multilayer graphene coating could provide up to 400 h of corrosion protection for Cu in NaCl solution [84]. Prasai compared the corrosion resistance of multilayer graphene coatings obtained by the CVD method and the mechanical transfer method. It was found that the multilayer graphene coating directly obtained by CVD had a 20 times higher corrosion resistance than bare Cu, while that of the multilayer coating obtained by the mechanical transfer method was four times greater than bare Cu because of the corrosion transport path left during the transformation [85]. Zhang et al. studied the corrosion of graphene-covered Cu in an atomic oxygen (AO) environment. SEM observation showed that after the sample was irradiated by AO, there was a white oxidation product on the surface of the bare Cu, and the surface of Cu covered by a single-layer graphene coating changed significantly. However, the surface of Cu covered by the multilayer graphene coating did not obviously change. The results indicate that the multilayer graphene coating has better oxidation resistance than the single-layer graphene coating. This finding is attributed to the fact that the matching defects between the multilayer graphene coatings overlap each other to form a steric hindrance effect, which inhibits the diffusion of O atoms in the vertical direction. Moreover, the barrier between the interlayers prevents the horizontal diffusion of O atoms [86]. Yu developed a graphene-polymer hybrid coating with two layers of single-layer graphene sandwiched between three layers of polyethylene, as shown in Fig. 8. The hybrid coating exhibited a better anti-corrosion effect than graphene or the polymer coating alone, which provided up to 120 days of protection for metals in simulated seawater environments [85].

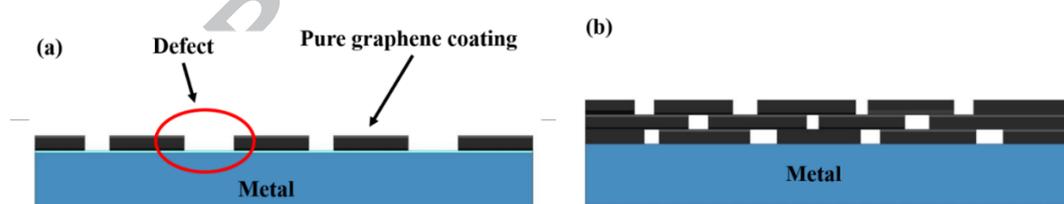


Fig. 7. Single-layer graphene and multilayer graphene

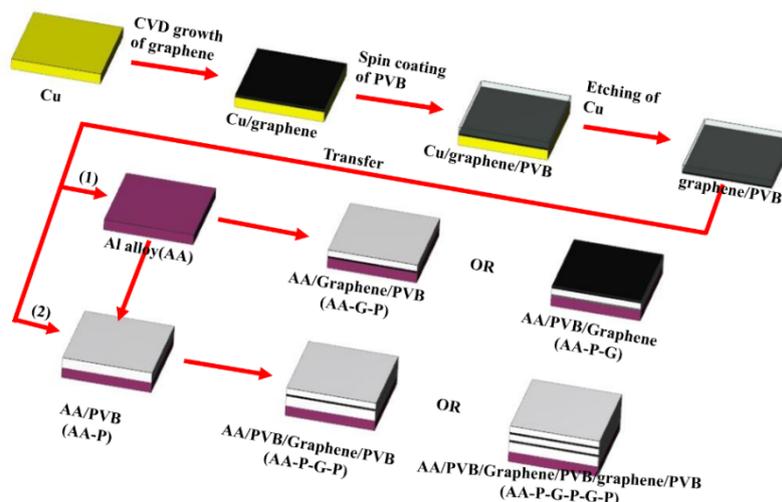


Fig. 8. Graphene-polymer hybrid coating

Fourth, atomic layer deposition (ALD) selectively passivates the graphene defects [19,66,87]. Ping selectively deactivated the defects of the graphene surface by ALD; that is, Al_2O_3 blocked the grain boundaries of graphene. Then, liquid was prevented from passing through these defects, and the corrosion resistance was improved. The corrosion current of Cu/1LG/ALD decreased with increasing ALD thickness. The 50-layer ALD coating (5 nm equivalent thickness) exhibited more corrosion resistance than the three-layer graphene coating, and as the number of ALD layers increased, the etching pit density decreased. The 160-layer ALD reduced the corrosion rate of bare copper by 99% and the Cu/1LG by 87% [66]. The above-mentioned method was used to reduce both the defect density of the pure graphene coating and the risk of corrosive media contacting the metal, which eventually provided long-term protection for the metal.

Finally, finding other 2D barrier materials, such as hexagonal boron nitride (h-BN), as a substitute for graphene is also a potential solution for metal corrosion. Researchers have already reported cases in which h-BN layers act as corrosion barriers for metals [88]. Liu et al. [89] demonstrated that h-BN possesses high-temperature oxidation resistance, which could protect nickel from oxidation up to 1,100 °C in the short term. Li et al. [90] heated Cu with a 7–8 nm (approximately 20 layers) h-BN coating in air for 100 h and found that the sample suffered less oxidation than bare Cu treated less than 2 h under the same conditions. Li et al. [91] tested the oxidation resistance of high-quality h-BN (1–4 layer) by heating in air. The oxidation temperature of single-layered h-BN is 700 °C, while that of graphene is only 250 °C. Shen et al. [92] compared the corrosion resistance of single-layered h-BN and graphene. These researchers found that both h-BN and graphene demonstrated excellent short-term protection. However, the h-BN coating maintained oxidation resistance for 160 days in air, while graphene failed in less than 80 days. The corrosion mechanism of BN/Cu and G/Cu samples is shown in Fig. 9.

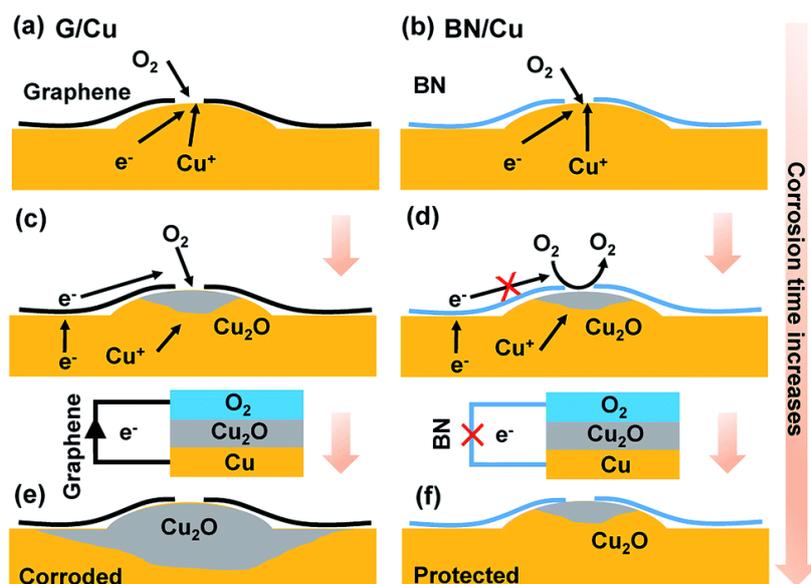


Fig. 9. Schematic diagrams of the corrosion mechanisms in the BN/ Cu and G/Cu samples. The defective sites in the (a) graphene and (b) BN samples allow the unprotected Cu to react with O_2 and eventually form oxides for both the G/Cu and BN/Cu samples. (c) The highly conductive graphene can transport electrons to oxygen atoms, working as the cathode in the electrochemical circuit. (d) The electrochemical circuit for the BN/Cu sample is open because BN is electrically insulating. Equivalent circuit for the (e) G/Cu and (f) BN/Cu samples[92]

3. Graphene composite anti-corrosion coating

Pure graphene anti-corrosion coatings have excellent anti-corrosion performance but still has many limitations in industrial applications. Once the pure graphene coating is damaged, the corrosion of the metal is accelerated. Moreover, it is difficult to scale up and industrialize this process under current technical conditions, and the preparation cost is relatively high. Another major use of graphene in the field of anti-corrosion involves the dispersion of graphene as filler particles into the coating matrix to form a graphene composite anti-corrosive coating. The graphene composite coating combines the strong adhesion properties of graphene and the film-forming properties of the coating matrix to improve the overall performance of the coating. Furthermore, the preparation method and coating process of the graphene composite anti-corrosive coating can be established based on the traditional coating production process, which shows good controllability and workability in industrial synthesis and applications. Graphene composite anti-corrosion coating will be a force in the future of new anti-corrosion coating materials. In this section, methods for improving the dispersibility of graphene in the coating matrix, the anti-corrosion performance of the coating, and the anti-corrosion mechanism are introduced. Based on these approaches, methods for optimizing the graphene composite coating are proposed.

3.1. Improvement in the dispersibility of graphene in the coating matrix

The pure graphene surface has no functional groups, a high aspect ratio, and van der Waals interactions, which make it easy to agglomerate in aqueous solution or organic matter. As a result, the graphene does not disperse well in the composite coating, resulting in a poor corrosion resistance, as shown in Fig. 10. Therefore, increasing the dispersibility of graphene in the coating matrix is important for enhancing the corrosion resistance of the coating.

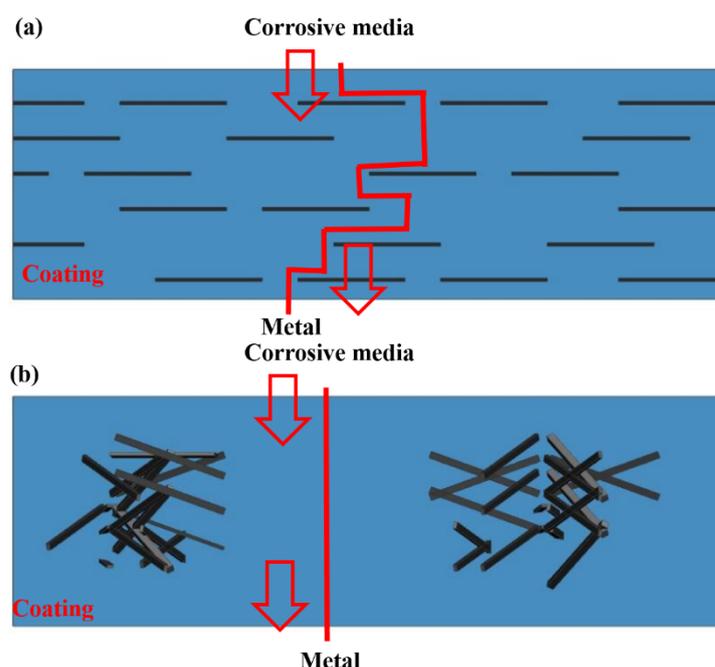


Fig. 10. Well-dispersed graphene (a) prolongs the permeation path of the corrosive materials. A poorly dispersed coating (b) has a short permeation path

At present, there are three main methods for improving the dispersibility of graphene in the coating matrix: physical dispersion, chemical modification, and NP-modified graphene surface. Physical dispersion methods are auxiliary measures for the dispersion of graphene in the coating; these methods include ultrasonic dispersion, high-speed magnetic stirring, shear emulsification, ball milling, and sanding dispersion processes. However, the dispersion effect is not obvious and is usually used to match the latter two methods. Therefore, in this section, two types of dispersion methods, namely, the chemical modification process and graphene surface decoration with NPs, are introduced in detail.

3.1.1. Chemical modification

The chemical modification of graphene is generally carried out using a chemical coupling agent. The coupling agent generally carries two types of functional groups: one is a hydrophilic group that can be combined with inorganic filler particles, and the other is an organophilic group that can react with the organic coating matrix. After modification, the edge or surface of the graphene is grafted with a long chain of a polymer, which makes graphene have better compatibility in the coating matrix. Simultaneously, the modified graphene acquires the characteristics of the polymer, which improves the overall performance of the graphene composite coating.

Silane coupling agents are one of the most common graphene modifiers. Li et al. modified GO using tetraethoxysilane (TEOS) with the aid of microwave radiation to obtain SGO. The modified SGO improved the compatibility with the silane matrix. The protective properties of the SGO/silane composite coating were significantly improved compared to the pure silane coating. When the content of SGO was 0.2 wt.%, the protection performance was optimal [93]. Parhizkar et al. modified GO using 3-(triethoxysilyl) propyl isocyanate (TEPI) and 3-aminopropyltriethoxysilane (APTES) to obtain IGO and AGO, respectively. It was found that the GO was unstably dispersed in the silane solution, while IGO and AGO were stably dispersed in the silane solution. [94]. This result is because the Si–OH of the silane coupling agent reacts with a reactive functional group of GO (such as carbonyl, hydroxyl, and epoxy groups) to form a Si–O–C covalent bond, which improves the bonding strength of the silane with GO [95]. Zhan et al. modified the GO/Fe₃O₄ hybrid NPs using a biomimetic polymer (dopamine) and silane (KH550). Rich amino groups and hydroxyl groups were introduced onto the surface of the particles, and the dispersion of NPs in EP was improved. At the same time, the interfacial tension between GO/Fe₃O₄ NPs and EP was increased by the chemical cross-linking reaction [96].

In addition to the silane coupling agents that are commonly used to modify graphene for higher dispersivity, scientists have also turned their attention to other chemical reagents. Dopamine (DA) is a type of nerve conducting media, and a poly-dopamine (PDA) film could be formed on the metal surface by self-polymerization [97,98]. Cui et al. modified GO with PDA, which improved the dispersion of GO in ethanol and the compatibility of GO in waterborne epoxy coatings. DA turned to PDA by self-polymerization and was adsorbed on the graphene surface by π - π interactions. Meanwhile, the functional groups of DA and PDA, such as catechol, amine, and imine, acted as the active sites for the covalent modification of GO [99] and promoted the reduction of GO, as shown in Fig. 11. After adding GO and GO-PAD into ethanol for 5 h, GO agglomerated, while GO-PAD remained well dispersed. The

photos of the dispersions are shown in Fig. 11(c) [100], and the results proved the benefit of PAD modification on the dispersibility of graphene.

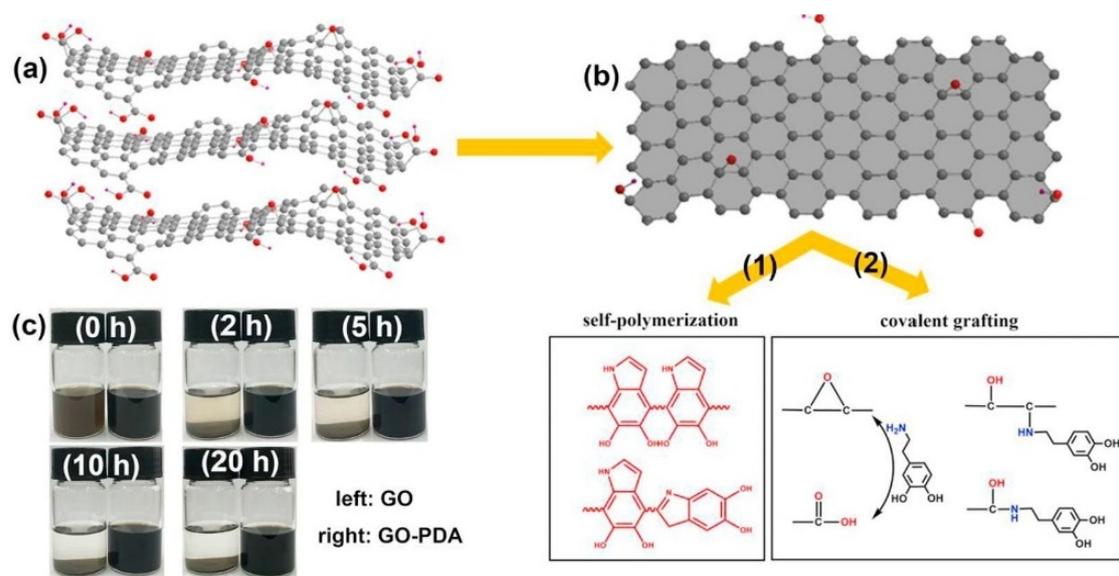


Fig. 11. The possible reactions for the modification of GO with PDA: (a) pristine GO, (b) GO-PDA, and (c) the dispersion of GO (left) and GO-PDA (right) in ethanol at various storage times [100]

Hu et al. modified GO and carbon nanotubes with 3-aminophenoxyphthalonitrile (3-APN). GO-CN was synthesized by acyl chloride and the amidation of the -COOH group on the GO surface with 3-APN. The synthesis routine is shown in Fig. 12(a). The characterization results showed that the grafting rate of 3-APN on the GO surface was 19%. The dispersibility of GO and GO-CN was tested in water and organic solvents. Due to the mass of the oxygen groups, GO has good dispersion in water but is hardly dispersed in ethanol and tetrahydrofuran (THF). The modified GO had good dispersion in water and maintained the stable dispersion in organic solvents, as shown in Fig. 12(b), which is attributed to the nitrile groups on the GO-CN surface. Therefore, the compatibility of graphene in the coating matrix may be improved by the polar interaction of the nitrile groups of GO [101].

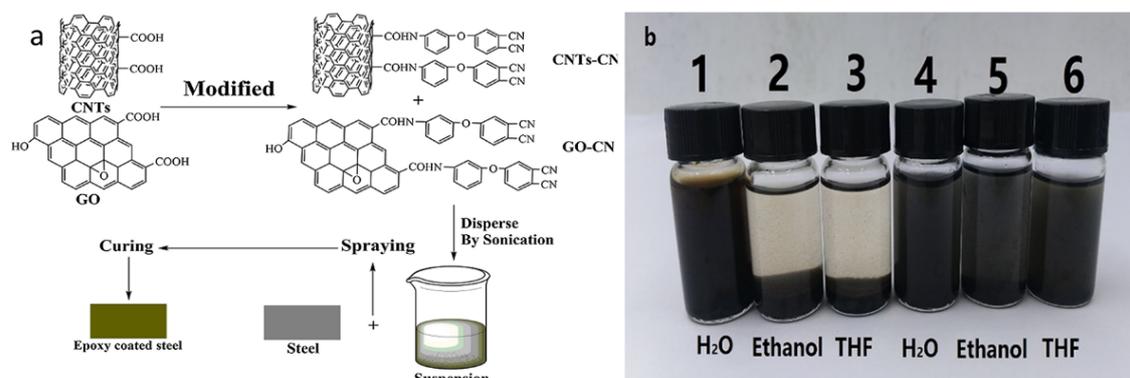


Fig. 12. (a) Synthesis schedule of the functional carbon nanotubes (CNTs) and graphene oxide/epoxy coating; (b) Digital photos of the graphene oxides (GO) (Nos. 1–3: pure GO, Nos. 4–6: modified GO) dispersed in different solvents [101]

3.1.2. Graphene surface decorating nanoparticles

To improve the dispersibility of graphene, acid oxidation is often used, which does have a good effect. However, at the same time, the structure of graphene is destroyed, and its inherent performance is also degraded [102]. The method of decorating NPs on the surface of graphene is very innovative, which can improve the dispersibility of graphene and also ensure the integrity of the graphene structure with fewer graphene defects. Currently, NPs, such as titanium dioxide, aluminium oxide, calcium carbonate, silicon dioxide and ferroferric oxide, are used to decorate the surface of graphene, which can increase the spacing between the graphene and the surface, decrease the agglomeration, and improve the corrosion resistance of the coating [96,103–107].

Yang et al. creatively introduced 1D multi-walled CNTs (MWCNTs) to effectively prevent the accumulation of multilayer graphene sheets (MGPs). Long and curved MWCNTs were attached to adjacent graphene sheets. The formed MGP/MWCNT structure showed a large contact area with the polymer, which improved the compatibility of graphene. When MGP or MWCNT is present alone in the THF solution, it can easily aggregate and precipitate. However, the MGP/MWCNT mixture has excellent dispersibility in solution, which proves that the introduction of 1D MWCNTs can effectively improve the dispersibility of graphene, as shown in Fig. 13 [102].

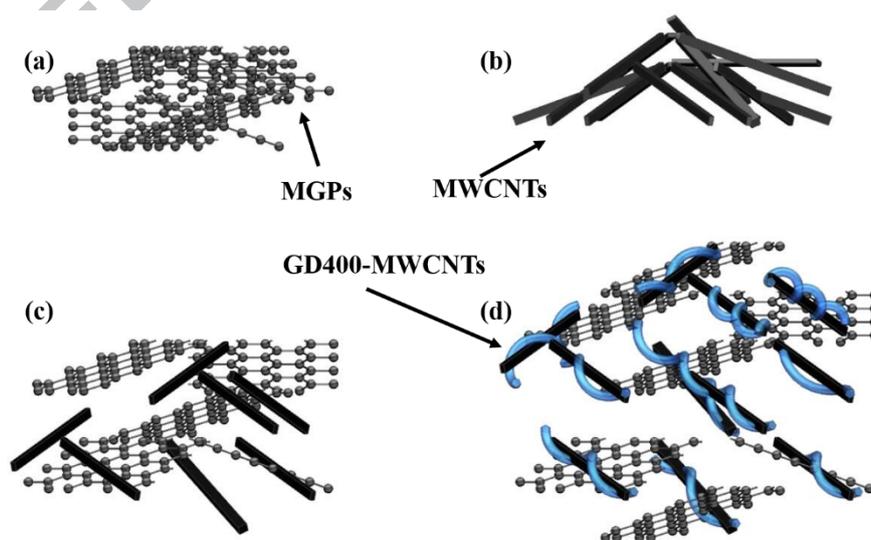


Fig. 13. Dispersion of MGP, MWCNT, and MGP/MWCNT in the THF solution

Liu et al. decorated nano-TiO₂ particles on the surface of graphene with the aid of 3-aminopropyltriethoxysilane (APS) to form a TiO₂-GO mixture, as shown in Fig. 14(a). Fourier transform infrared (FTIR) spectra showed the Si-O-Ti peak at 875 cm⁻¹, which indicated that GO was covalently modified by TiO₂. GO carries oxygen-containing functional groups and has good dispersibility in water. However, it undergoes easy aggregation and precipitation in the organic solution. After the GO was modified by TiO₂, it could be well dispersed in the organic solution, as shown in Fig. 14(b). This process is ascribed to the fact that when TiO₂ is decorated onto GO, OH and COOH are reduced, and TiO₂-GO becomes lipophilic. After 3 h, the TiO₂-GO was still well dispersed in the organic solvent. Subsequently, TiO₂-GO was modified with 3-glycidoxypropyltrimethoxy silane (GPTMS). The SEM results showed that modification with GPTMS further improved the dispersibility of graphene and increased the compatibility of TiO₂-GO in the coating matrix [108].

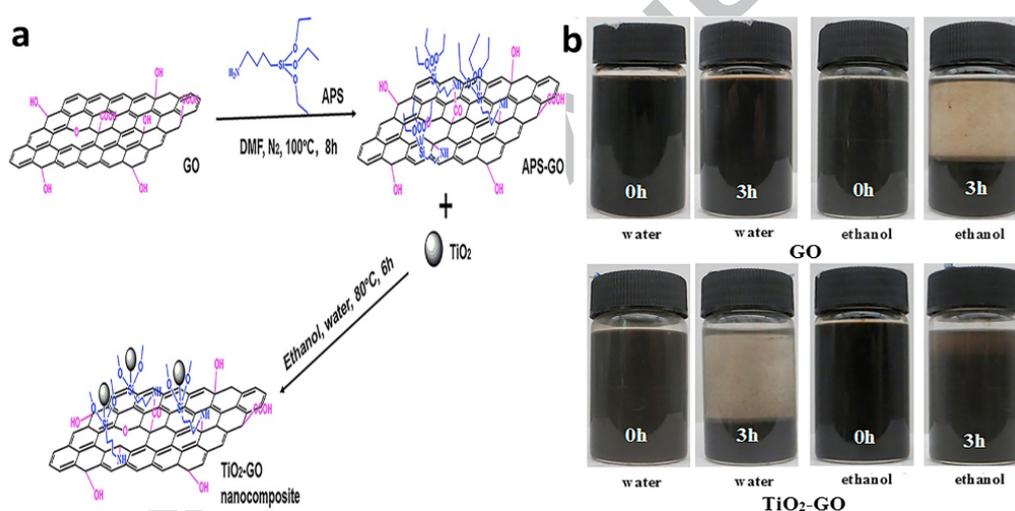


Fig. 14. (a) Synthetic reaction process diagram of the TiO₂-GO nanocomposite and (b) the visual illustration of the GO and TiO₂-GO suspension in water and ethanol at different times [108]

3.2. Anticorrosion performance of the graphene composite coating

According to the type of chemical bond between graphene and other materials, the previous section was divided into covalent and non-covalent modifications. This section discusses the corrosion behaviour of coatings incorporated with modified graphene [109]. Typically, the bonding of polymer chains, small molecules or nanoparticles on graphene represents the covalent modification [94,96,108,110,111], while the non-covalent modification of graphene occurs via the interaction of π - π bonds, hydrogen bonds and ionic bonds [112–116]. Covalent modification is conducive to maintaining the chemical stability and mechanical properties of graphene, while non-covalent modification facilitates the

excellent conductivity and ultra-high specific surface area [109]. Therefore, researchers should choose the appropriate modification methods according to their demands.

Silane has physical barrier properties and is often used as a pretreatment for metals. When silane is hydrolysed, the produced Si–OH forms a hydrogen bond with the hydroxyl group on the metal surface, which improves the adhesion of the coating substrate with the metal substrate. However, when the solution evaporates, many micropores are formed, the corrosive media can contact the metal through the micropores, and the metal is corroded [93]. Parhizkar et al. covalently functionalized GO using 3-(triethoxysilyl) propyl isocyanate (TEPI, IGO) and 3-aminopropyltriethoxysilane (APTES, AGO). The obtained IGO and AGO reduced the porosity of the silane structure pretreated on the metal surface and increased the adhesion strength of the silane coating with the top epoxy coating. Through salt spray testing, it was found that the amount of corrosion products and blisters around the scribing lines of the SC-AGO/EP and SC-IGO/EP coatings was small. This finding is because the graphene composite coating is in close contact with the metal, which hinders the propagation of the corrosive media in the coating, and as a result, the generation of corrosion products and blisters is reduced [94].

Liu et al. grafted imidazole ions onto a GO surface by a simple grafting reaction to obtain the modified graphene IL-GO, which was not only dispersible in water but was also uniformly dispersed in the epoxy-based aqueous coating matrix. After adding 0.5 wt.% of IL-GO to the epoxy-based aqueous coating, the anti-corrosive ability of the metal was remarkably improved. The scanning vibrating electrode technique (SVET) was used to study the local electrochemical behaviour of the graphene composite coating on the steel electrode, and the SVET maps. For pure epoxy-coated steel, the average anode current of the scanning area increased from $3.10 \mu\text{A}\cdot\text{cm}^{-2}$ (1 h) to $4.75 \mu\text{A}\cdot\text{cm}^{-2}$ (30 h), indicating the dissolution of the anode. The anode current of the IL-GO composite coating declined as a function of time and reached a minimal value ($2.20 \mu\text{A}\cdot\text{cm}^{-2}$) at 30 h, suggesting the anticorrosion property of the IL-GO composite coating. The metal under the protection of the pure epoxy coating and the epoxy coating with 0.5 wt.% rGO showed the presence of numerous corrosion products at the scratch after the 100 h salt spray test, while the scratches on the metal protected by the graphene composite coating were still relatively clean after the 300 h salt spray test. The pull-off test of the three samples showed that the IL-GO composite coating had the highest bond strength, which reduced the peeling of the coating and enhanced the anti-corrosion effect [111].

The anti-corrosion performance of coatings incorporated with graphene is simply noncovalently functionalized by intermolecular forces. The dispersal of graphene in the epoxy matrix could be promoted by π – π interactions of 2-aminothiazole (PAT). Qiu et al. modified graphene with 2-aminothiazole (PAT) to prepare a PAT-G-EP graphene composite

coating, and the schematic diagram is shown in Fig. 15(a). The barrier properties of the pure epoxy and the graphene composite coatings were evaluated by water absorption and electrochemical testing in a 3.5 wt.% NaCl solution. The R_p and R_{ct} in EEC usually represent the barrier properties of coatings. The value of R_p of coating loaded with 0.5 wt.% graphene is always higher than that of other coatings, while the coating with an excessive content of graphene (1 wt.%) showed poor corrosion resistance, as shown in Fig. 15(b-e). After soaking for 240 h in the solution, the water absorption of the PAT-G-EP graphene composite coating with 0.5 wt.% graphene was less than 0.5%, which was reduced by 89% compared to pure epoxy coatings. The composite coating maintained good corrosion resistance after immersion in a 3.5 wt.% NaCl solution for 80 days. At the same time, the wear rate of the composite coating with 0.5 wt.% graphene was the lowest, which was 69.48% lower than that of the pure EP [114].

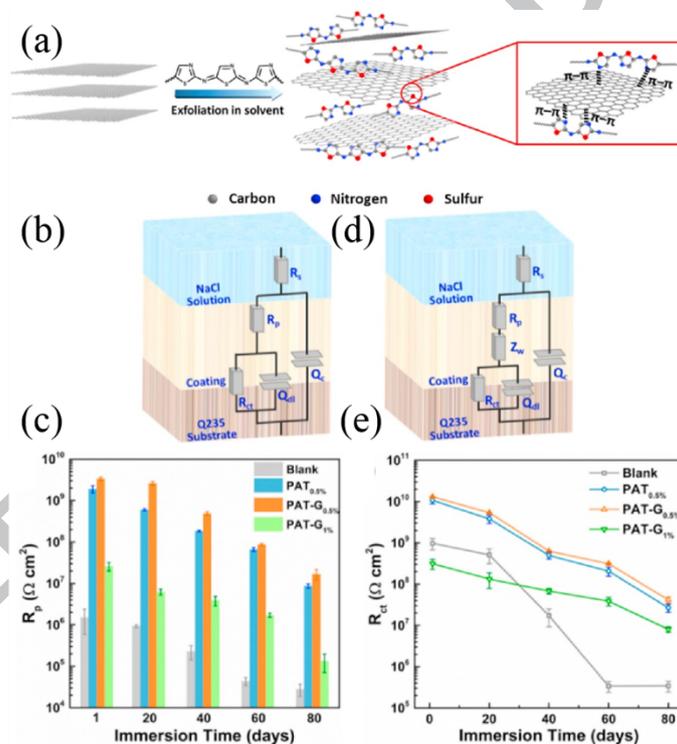


Fig. 15.(a) Schematic representation of the preparation of PAT-G hybrids; (b), (c) Electrical equivalent circuit models and the evolution of the (d) R_p and (e) R_{ct} values with immersion in the 3.5 wt % NaCl solution [114]

Ding et al. tested the $\pi-\pi$ interactions between the hydroxyl epoxy phosphate monomer (PGHEP) and graphene using Raman spectra, ultraviolet-visible spectra (UV-vis), and X-ray photoelectron spectroscopy (XPS). The non-covalent graphene coating modified by PGHEP has excellent dispersibility within the water and coating matrix. The EIS and salt spray tests were used to evaluate the corrosion resistance of the coatings. As shown in Fig. 16, the waterborne epoxy coating with graphene contents of 0.5 wt.% (PGHEP-G_{0.5%}/WEP)

and 1 wt.% (PGHEP-G_{1%}/WEP) exhibits higher values of R_c and R_{ct} . The reason for the promotion of the corrosion resistance is that PGHEP facilitated the formation of the passivation phosphate film on the substrate metal, and the modified graphene hindered the penetration of corrosive media. After immersion for 7 days, all the coated samples reached stable water absorption, as shown in Fig. 16(d). When immersed for 15 days, the water absorption of WEP and PGHEP /WEP reached 0.83 wt.% and 0.65 wt.%, respectively, while that of PGHEP-G_{0.5%}/WEP (0.52 wt.%) and PGHEP-G_{1%}/WEP (0.55 wt.%) remained low. Moreover, the water contact angle of PGHEP-G_{0.5%}/WEP reached 83.5°, while the water contact angle of WEP was 50.6°. The formation of hydrophobic phosphate film and incorporation of graphene reduced the water absorption and hydrophobicity of the coatings [115].

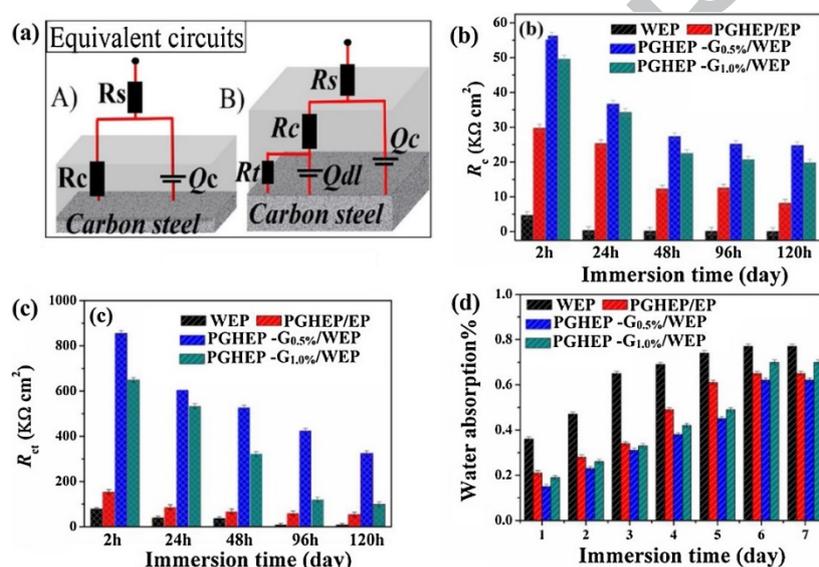


Fig. 16. (a) The equivalent circuits; (b) the fitting results of R_c ; (c) the fitting results of R_{ct} ; and (d) the water absorption of WEP, PGHEP/WEP, PGHEP-G_{0.5%} and PGHEP-G_{1%} coatings as a function of time in water at room temperature [115]

Compared to the covalent surface modification, the non-covalent surface modification of graphene is easy to operate and does not require complex chemical reactions. Interestingly, graphene modified by covalent and non-covalent surface modification could be incorporated in the coatings at the same time, and the different types of graphene could enhance the corrosion resistance in a concerted manner. Zhan et al. modified the GO/Fe₃O₄ hybrid NPs using the biomimetic polymer dopamine and silane (KH550). The dopamine adsorbed onto the graphene surface by π - π interactions, while KH5560 modified the graphene covalently. The introduction of abundant amino groups and hydroxyl groups onto the surface of the particles led to an increase in the dispersion of the NPs in the EP. At the same time, the interfacial tension between the GO/Fe₃O₄ mixed NPs and EP was increased by a chemical cross-linking reaction. Therefore, the modified GO/Fe₃O₄ (GO-Fe₃O₄-

KH550/DA) epoxy coating was more resistant to corrosion than GO-EP and unmodified GO/Fe₃O₄-EP. When the content of mixed NPs was 0.5 wt. %, the micro-hardness and corrosion resistance of the composite coating were optimal. H₂O and O₂ are the main causes of steel corrosion. There are fine channels inside the pure epoxy coating, and H₂O and O₂ easily penetrate through these channels. After the addition of the graphene derivative, the graphene composite coating effectively prevents the penetration of the corrosive media, and the H₂O and O₂ permeation channels are blocked, as shown in Fig. 17. Graphene with good dispersibility in the graphene composite coating forms a physical barrier in the coating and hinders the corrosive media. Furthermore, the modified graphene makes the bonding between the coating substrate and the protective metal more compact. The gap between the coating and the metal is reduced, and the peeling rate of the coating is significantly reduced [96].

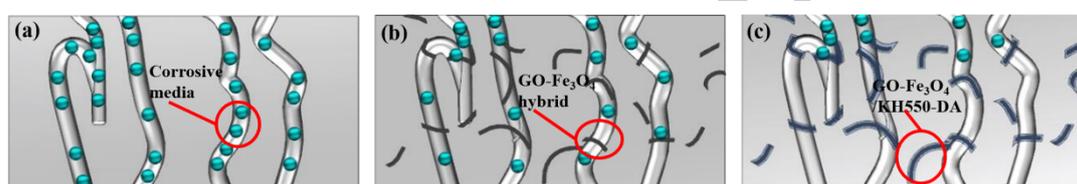


Fig. 17. (a) Pure epoxy coating, (b) the anti-corrosion mechanism of unmodified GO-Fe₃O₄ / EP graphene composite coating, and (c) the modified GO-Fe₃O₄ graphene composite coating

3.3. Anti-corrosion mechanism of the graphene composite coating

The graphene composite coating has good anti-corrosion performance mainly due to the following two aspects. First, graphene acts as a "barrier" in the coating, which could hinder the penetration of the corrosion media and propagation of cracks. Second, graphene becomes the channel of electron flow between the anode particles and the substrate in the coating, which enhances the protective effect of the sacrificial anode.

3.3.1. The "barrier" effect of graphene

(1) Graphene impedes the penetration of corrosive media

For pure polymer coatings, corrosive media could penetrate into the substrate along the thickness of the coating. Once the corrosive media reach the interface of the coating-metal, the corrosion reaction occurs. Graphene is composed of sp²-hybridized carbon atoms, and its electron density on the aromatic ring is high, which could block all molecules [22], as shown in Fig. 18. Thus, the specific structure of graphene achieves its impermeability. During the infiltration process of graphene embedded coatings, graphene could provide excellent

shielding protection by prolonging the infiltration path. Thus, the corrosion resistance as well as the life span of the coating can be greatly improved and extended [117–119].

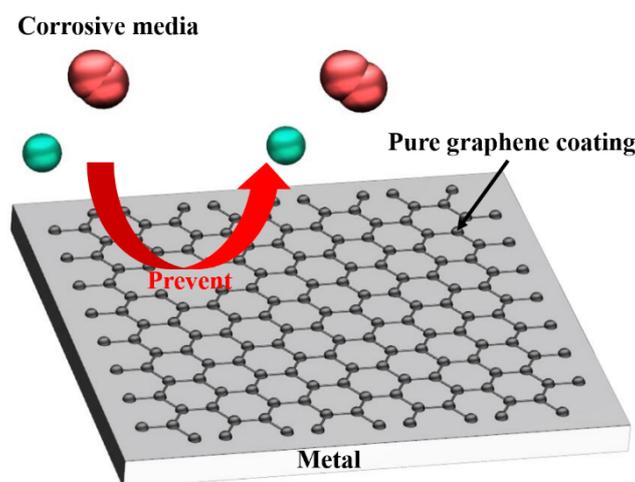


Fig. 18. Graphene acts as an anti-corrosion barrier to prevent oxidation

In this paper, the barrier effect of graphene in the coating is further explained using an existing mathematical model. A relatively simple mathematical model was chosen for analysis, namely, the Nielsen predictive model [120]. In an atmospheric environment, the infiltration process of corrosive media, such as O_2 and H_2O , in the graphene composite coating is controlled by a diffusion dissolution mechanism. According to Fick's law and Henry's law, equation (1) can be obtained:

$$Q = DSAt\left(\frac{\Delta p}{t_m}\right) \quad (1)$$

where Q is the amount of leakage through the coating (nm^3), D is the diffusion coefficient of the corrosive gas in the graphene anti-corrosion layer, S is the solubility coefficient of the corrosive gas in the graphene anti-corrosion coating, A is the effective area of gas permeation, t is the permeation time (s), and Δp is the osmotic pressure difference (nmHg).

According to equation (1), the permeability coefficient of the graphene anticorrosive coating can be obtained:

$$P = D \times S \quad (2)$$

It is assumed that the presence of particles does not affect the local properties of the matrix. The filler has good compatibility with the matrix without voids. The solubility of the corrosive media in the coating can be expressed as:

$$S = S_0(1 - \phi) \quad (3)$$

where S_0 is the osmotic solubility of the pure polymer, and ϕ is the volume fraction of the graphene particles in the matrix. Diffused molecules cannot pass directly through the particles and must pass through the coating along a more tortuous path. The diffusion rate is slow and can be expressed by equation (4):

$$D = \frac{D_0}{\tau} \quad (4)$$

$$P = P_0 \times \frac{1 - \phi}{\tau} \quad (5)$$

where D_0 is the diffusion coefficient of the pure polymer coating, τ is the graphene curvature factor, which is related to the shape and volume fraction of graphene, and P_0 is the permeability of the pure polymer matrix [12–14].

Nielsen [121] simplified the graphene composite coating model. It is assumed that the graphene in the coating is uniformly ordered and parallel to the surface of the coating. Based on model, the Nielsen prediction model is proposed, and the equation is shown in (6):

$$\tau = 1 + \frac{\alpha\phi}{2} \quad (6)$$

where α is the aspect ratio of graphene. This model clearly proved that the tortuosity of the permeation path of corrosive media in the graphene composite coating is related to the graphene volume fraction and the aspect ratio. Graphene has a high aspect ratio, which means that when adding nanoparticles of the same volume fraction, the corrosive media has a more tortuous path and a lower permeability in the graphene-added coating than in other nanoparticle-based coatings. Additionally, the higher aspect ratio of the graphene composite coatings is also advantageous over other nanocomposite coatings [122,123]. However, this model has some limitations. Through post-experimental experiments, it was found that when the volume fraction is less than 0.01, the model can accurately predict the permeability of the coating. When the volume fraction is greater than 0.01, agglomeration occurs, and the prediction result becomes unreliable. Many scientists have revised this model, which renders a more accurate prediction model for the graphene composite coating [124–128].

(2) Graphene hinders crack propagation in the coating

Cracks are unavoidable during the preparation and use of the coating. These tiny cracks are often an excellent entry point for corrosive media to invade the metals. Due to the presence of these fine crack defects, the corrosion resistance of the coating is reduced. If the

crack continues to expand, then the crack extends deeper, and the crack area becomes larger. As more corrosive media enter the coating, severe localized corrosion can occur. Graphene can play a key role in increasing the coating toughness, which hinders the expansion of cracks and reduces the penetration of the corrosive media.

The mechanisms of graphene hinder crack propagation could be summarized as consuming the crack growth energy and affecting the crystallization of polymers in the composite coatings [129]. When the crack in the coating reaches the interface of the graphene-matrix, the opening displacement of the crack tip is smaller than the size of the graphene; thus, the crack may be pinned without expanding. The tip stress during crack propagation will cause the debonding of graphene. Microcracks are formed around the graphene, or cracks appear in the graphene itself. The formed microcracks consume a large amount of the original fracture energy. If external forces continue to increase, then crack deflection may occur through the broken graphene [130–133]. The cracks deviate from the original expansion direction and prolong the crack propagation path. Therefore, the crack propagation resistance is increased. The graphene fracture also absorbs a certain amount of fracture energy and delays crack propagation in the coating [133,134]. Furthermore, the addition of graphene to the crystalline and semi-crystalline polymers can also affect the behaviour of polymer crystallization. The polymer can be crystallized in the direction of high toughness. The toughness of the polymer matrix could be improved by increasing the number of crystals and changing the crystal form [129,135,136]. Zhang et al. added fully exfoliated octadecylamine-functionalized graphene (ODAG) to transparent poly(lactic acid) (PLA) to prepare a nanocomposite film. Compared with pure PLA, it was found that its tensile toughness was improved by a factor of 3. On the one hand, it was found through tensile tests that the ODAG and PLA interfaces slipped and consumed a large amount of fracture energy. On the other hand, since PLA is a semi-crystalline polymer, the crystallization behaviour will affect the toughness of PLA. The addition of graphene to PLA significantly increases the intensity of the diffraction peak. The degree of crystallization is improved, and the crystal order is improved. Graphene-based PLA exhibits higher crystallinity and smaller crystal size than pure PLA.

3.3.2. Graphene enhances the role of the sacrificial anode

Zinc-rich coatings work well as sacrificial anodes, requiring efficient electron paths between the zinc particles and the metal substrate. The binder in the coating is often not electrically conductive. This effect can result in many isolated zinc particles in the coating, which are not in contact with the metal substrate. Thus, it is difficult to provide effective protection for the metal substrates[137–141]. The addition of graphene in the coating serves two purposes: acting as a cathode and conducting the zinc powder particles.

Graphene is the cathode of the zinc powder particles. The addition of a large amount of graphene in the coating adds a large amount of cathode to the coating. Therefore, the external electrolyte can react when it contacts the graphene and zinc powder particles. The electrolyte does not need to continue to permeate, seeking a cathode for the zinc powder particles. At the same time, the generated insoluble corrosion product fills the permeation channel in time, hindering further penetration of the electrolyte solution and improving the corrosion resistance of the coating.

In addition, the polymer in the coating hinders electronic communication. The resulting corrosion products are also non-conductive, resulting in more zinc powder particles being isolated, reducing the utilization of zinc powder. As an excellent conductor, graphene has become a bridge for the electronic communication between zinc powder particles. Many isolated zinc particles are in electronic communication with the interface zinc or metal substrate by forming a large conductive network in the coating, as shown in Fig.19. Then, the sacrificial anode reaction continues to occur[141].

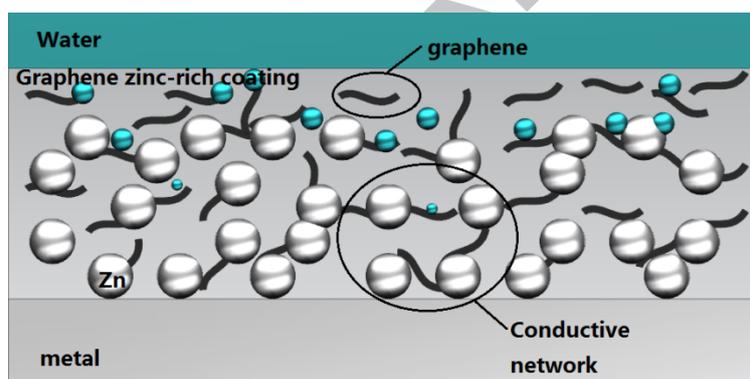


Fig. 19. Formation of a conductive network between graphene and zinc powder. The cathodic protection and anti-corrosion effect of zinc-rich coating are improved

3.4. Optimization of the graphene composite coating

3.4.1. Orderly arrangement of graphene

The corrosion resistance of the graphene composite coating is affected not only by the dispersibility of graphene in the coating but also by its orientation. However, in most of the studies, graphene has been randomly dispersed in the composite coating rather than being highly ordered, and thus, a better anticorrosion effect was not obtained. There are many predictive models for the barrier properties of composite coatings. In the improved Nielsen model, the orientation of graphene was considered. In this model, the following three cases were included: When $S = 1$ ($\vartheta = 0^\circ$) (S indicates the parameter corresponding to the orientation of the graphene sheet), the graphene sheet is parallel to the base metal. When

the graphene layer is aligned, the permeability of the corrosive media is the lowest. When $S = 0$ ($\vartheta = 54.74^\circ$), the graphene sheets are randomly distributed in the coating. When $S = -1/2$ ($\vartheta = 90^\circ$), the graphene sheets are perpendicular to the base metal and do not block the diffusion of corrosive media, as shown in Fig. 20 [120].

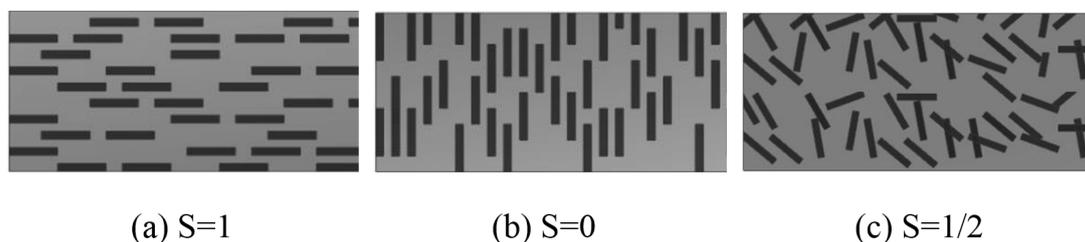


Fig. 20. Different orientations of graphene in the graphene composite coating

Through the above-mentioned empirical model, it has been shown that when graphene is arranged in order, the barrier ability of the graphene composite coating to the corrosive media is improved [50,142]. Jiao et al. added magnetic NPs (Fe_3O_4) to the surface of graphene nanosheets (GNP) by wet chemical coprecipitation. Then, under a low magnetic field (40 mT), $\text{Fe}_3\text{O}_4/\text{GNP}$ was self-aligned in the epoxy resin to form a highly ordered graphene composite coating. SEM images showed that the magnetic graphene (m-GNP) was parallel to the direction of the magnetic field. For highly ordered composite coatings prepared using 1.0 wt.% m-GNP, the gas barrier performance was one order of magnitude better than pure EP coatings and increased by 65% with respect to the same amount of GNP randomly arranged in the composite coating [143]. Li et al. modified graphene using ethylene-vinyl alcohol copolymer (EVOH) and boric acid (BA). When the BA content was 15% and the graphene content was 5%, the EVOH/15BA/5GO graphene composite coating was prepared. Through the cross-sectional FESEM image of the coating, Li observed a layered structure in which the graphene sheets were almost parallel to the substrate. This finding indicates that the graphene in the coating is uniformly dispersed and highly oriented. This behaviour is attributed to the increase in the interfacial interaction between graphene and EVOH due to borate ions. The EVOH/15BA/5GO composite coating exhibited the lowest O_2 permeability and an ultra-low corrosion rate of $3.43 \times 10^{-3} \text{ mm y}^{-1}$ [144]. Li et al. prepared a TGO/PU composite coating and found by SEM and TEM observation that self-alignment occurred when TGO was 0.4 wt.%. That is, TGO was parallel to the substrate in a 2D arrangement, which provided a long and tortuous path of penetration for the corrosive media, as shown in Fig. 21. The EIS test proved that the composite coating could improve the corrosion protection of the metal in the electrolyte for up to 96 h [145].

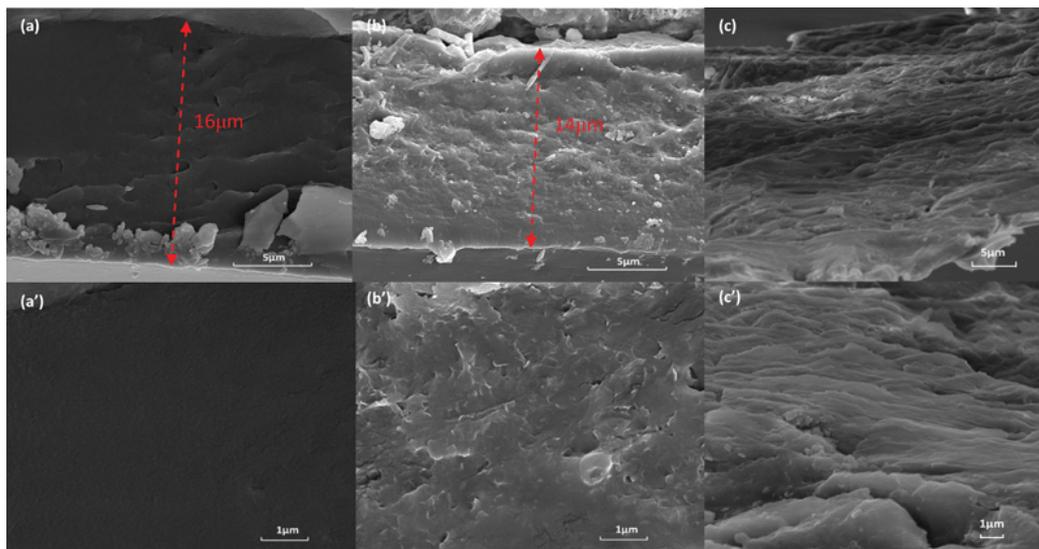


Fig. 21 (a) and (a'). Pure PU coatings exhibit a relatively smooth fracture surface; **(b) and (b')** when the TGO content is 0.2 wt.%, the TGO is randomly distributed; and **(c) and (c')** the TGO content was increased to 0.4 wt.%, and TGO is aligned in parallel with the EG substrate [145]

3.4.2. Conversion of graphene properties

Graphene acts as a filler in composite coatings and a barrier to corrosive media. However, graphene does not provide longer protection due to its corrosion promotion effect. A galvanic couple is formed between the graphene and the metal substrate. Unfortunately, graphene acts as a cathode for most metals, and thus, the presence of graphene accelerates metal corrosion and leads to galvanic corrosion. In general, polymers are not electrically conductive, and there is no concern that the polymer coating will form galvanic corrosion with the substrate. However, after the addition of graphene, the conductivity of the polymer coating increases by several orders of magnitude [146], and there is still a risk of galvanic corrosion [147]. Regarding the above-mentioned issue, there are three ways to optimize the corrosion resistance of graphene coatings. One method is the reduction in the conductivity of graphene by chemical modification or encapsulating graphene with an insulating material to avoid a galvanic coupling between the graphene and metal. The second method is converting graphene into an anode, for example, by adding a more active anode material (Zn) to the coating. The third approach is searching for alternatives that possess stable electric insulation and other properties similar to graphene.

Ding et al. synthesized graphene and a furan epoxide monomer (FdE) to form non-conductive graphene (FmG) by a Diels–Alder reaction. Graphene was encapsulated by an insulating polymer FdE, which does not have electrical conductivity, good dispersibility, and compatibility with the coating. After the sample was immersed in an aqueous solution for

120 days, the coating was peeled off from the surface. The SEM observation showed that the corrosion of the sample covered by pure epoxy coating (FmG_0) was pit corrosion, and the other samples covered by the graphene composite coating showed no signs of corrosion except for the sanding marks. Atomic force microscopy (AFM) images show that the pure epoxy coating failed to provide corrosion protection to the substrate, and deep pits appeared on the surface, while the substrate protected by the graphene composite coating was flat and not corroded. Through electrochemical tests, the sample still maintained good corrosion resistance [146]. Sun et al. wrapped graphene with SiO_2 to form graphene- SiO_2 nanosheets (GSs). SiO_2 was used as a barrier between the graphene and metal to prevent direct contact. The SEM and TEM characterization of the GSs showed that graphene was uniformly covered with SiO_2 and no bare graphene was found. At the same time, the 3D conductive network of graphene was destroyed, forming a poorly conductive GS structure, which prevented the graphene from promoting corrosion. When the coating was damaged, graphene could not promote corrosion [147]. Doping with electron dopants can also reduce the conductivity of graphene. Ding et al. synthesized B-doped graphene (BG) and added it to an aqueous polyurethane (PU) resin. These researchers found that the corrosion resistance of the coating is greatly improved. This improvement is because the high insulation properties of BG inhibit the galvanic reaction [148].

The zinc-rich epoxy coating protects the metal by the sacrificial anode reaction of Zn [149]. However, polymers do not have good electrical conductivity in the coating. Therefore, to enhance the continuity of electron flow between Zn and metal, the Zn content is often greater than 80%. In contrast, high levels of Zn reduce the toughness and adhesion properties of the coating, and increase the viscosity resulting in poor sprayability [23,150]. However, only a small amount of Zn is consumed as an anode, and most of the Zn is not consumed until the coating fails, resulting in a considerable waste of the zinc-rich epoxy coating. Hayatdavoudi et al. added an appropriate amount of graphene to the zinc-rich epoxy coating to enhance the continuity of electron flow between the zinc particles and the metal, as shown in Fig.19. In this case, more zinc particles are activated, and its utilization is increased. At the same time, the barrier effect of graphene leads to an increase in the corrosion resistance of the coating. Ding et al. prepared a zinc-rich epoxy coating containing graphene and discussed the influence mechanism of graphene on the coating by EIS. The use of the zinc-rich epoxy coating containing graphene is divided into five stages: initial shielding, wavering, cathodic protection, shielding, and failure. The shielding effect of graphene slows down the penetration of corrosive media in the coating, which delays failure phases and increases the duration of cathodic protection. At the same time, the zinc particles and metals are connected, which increases the electron transport channel and improves the utilization of zinc particles [141].

The seeking of insulating graphene-like materials opens a new way to solve the galvanic corrosion associated with graphene. To date, hexagonal boron nitride (h-BN), also called “white graphene”, is the most promising insulating 2D barrier layer. A single layer of h-BN is electrically insulated and possesses outstanding impermeability, mechanical properties, and thermal stability [151]. Yi et al. synthesized 2.5 nm thick boron nitride nanosheets by vacuum filtration on Nylon. The barrier and bonding effects of h-BN protect the polymer from oxygen-atom corrosion [152]. Cui et al. dispersed water-soluble h-BN in an epoxy coating using a carboxylated aniline trimer as a noncovalent dispersant. The uniform distribution of the h-BN layers significantly enhanced the water barrier property and corrosion resistance of the coating at a concentration of only 1 wt.% [153]. Their team also dispersed h-BN as a nanofiller in tetrahydrofuran using poly (2-butyl aniline) (PBA) as a dispersant. By dispersing h-BN in epoxy, the toughness of epoxy was improved, and the “labyrinth effect” of h-BN prolonged the penetration of the corrosive media. Moreover, the coating structure became denser because the metal surface was passivated by PBA. Therefore, the h-BN reinforced epoxy coating could provide stable protection in the long-term [154]. However, the synthesis of h-BN is more expensive than preparing graphene [151], and researchers have been working on finding inexpensive and large-scale synthesis processes for h-BN and have been seeking other graphene-like 2D barrier materials.

4. Conclusion and outlook

Pure graphene coatings can isolate corrosive media from the base and provide effective protection for metals. Currently, CVD has been mainly used to synthesize graphene in the laboratory due to its potential for mass production. However, defects in graphene may accelerate the corrosion of substrate metals in the long term. The local oxidation of graphene will reduce its mechanical strength and affect its service life. Therefore, it is necessary to improve the CVD preparation process to fabricate pure graphene coatings with a large area, low defect density, and strong resistance to mechanical damage. Furthermore, it is necessary to strengthen the research of the physical vapor deposition (PVD) method to grow graphene. The PVD method is susceptible to controlling the number of graphene layers, which eliminates the dependence of graphene layer transfer. This method uses amorphous carbon as a carbon source, which greatly reduces the production expense.

Graphene composite coatings possess more satisfying corrosion resistance than conventional coatings because of its “barrier” effect. Graphene inhibits the penetration of corrosive substances and, on the other hand, the propagation of cracks. In terms of zinc-rich coatings, graphene could also enhance the protection of sacrificial anodes. Based on the above mechanisms, graphene enhances the corrosion resistance of coatings. At present, the protection mechanism of graphene composite coatings still requires further research. In the

future, the current and potential distribution of metals under the protection of graphene composite coatings should be explored using micro-zone testing techniques, such as tow electrodes and microelectrodes. Moreover, through artificial acceleration experiments, the failure derivation mechanism of the graphene composite coating should be clarified.

The dispersion and orderly alignment of graphene in coatings are critical to its shielding protection. To increase the dispersion of graphene in coatings and its stable existence in polymer matrices, graphene modification approaches can be used. However, the covalent bond modification damages the original structure of graphene. At the same time, these chemical agents are highly toxic and use large dosages, which can easily cause pollution and endanger the health of workers. Therefore, more systematic explorations are needed to develop green and environmentally friendly modification methods and pharmaceuticals that can retain the original structure of graphene to the utmost extent to ensure dispersion and reduce environmental pollution and health hazards. Non-covalent modifications of graphene, such as π - π stacking, ion bonding, and hydrogen bonding, are good approaches.

Improving the ordered arrangement of graphene in coatings is also a hot topic. The ordered arrangement of graphene in the coating matrix is more conducive to prolonging the permeation path than a random arrangement, thus increasing the barrier to the penetration of corrosive substances in the coating. In some studies, coatings of graphene parallel to a metal substrate were prepared; however, the mechanism of the ordered distribution of graphene in the coating has not been studied in depth. The process of dispersing graphene cannot be effectively controlled, and the process for preparing a highly ordered oriented graphene composite coating has not yet been reported. At the same time, the ordered distribution of graphene in the current research does not reach a highly ordered distribution in the ideal sense but only achieves a relatively uniform orientation. Ordered distribution can significantly improve the performance of graphene composite coatings, which will be a hot research topic in the future.

Compared to graphene solvent-borne anticorrosive coatings, graphene waterborne anticorrosive coatings contain less toxic heavy metals and volatile organic compounds (VOCs). Therefore, graphene waterborne anticorrosive coatings have received increasingly more attention. Thus, the development of water-based coatings has become an important development direction for heavy anti-corrosion coatings. There are still some technical difficulties associated with graphene waterborne coatings that have not yet been solved. Graphene waterborne anticorrosive coatings with high quality are difficult to form, and their film-forming properties and abrasion resistance are also poor. Owing to the presence of residual water-based groups in the waterborne anti-corrosion coating, it has poor shielding ability against corrosive media such as water and oxygen. Since the surface tension of water is greater than the critical wetting surface tension of the pigment, it is difficult for the

waterborne coating to achieve the high infiltration and dispersion of pigments, such as graphene. Therefore, the suitable modification of graphene and the matching of graphene with the appropriate corresponding waterborne coating system to improve the dispersibility and compatibility of graphene in coatings are still highly desirable. The optimum amount of graphene in waterborne coatings and an enhancement of the shielding ability of graphene aqueous coatings for corrosive media, such as water and oxygen, are worth studying.

In addition, the search for graphene-like 2D barrier materials is also an urgent matter. Due to the conductivity of graphene, galvanic corrosion is an undeniable problem that is associated with coatings incorporated with graphene. Electrically insulated 2D materials that have begun to emerge, such as h-BN, could fundamentally avoid galvanic corrosion. Therefore, it is necessary to further study h-BN and find an economic synthesis routine for scaled production. Moreover, it is meaningful to develop new materials and broaden the category of graphene-like materials.

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Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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Highlights

- Application of graphene coatings to metal anti-corrosion is reviewed.
- Corrosion resistance and existing problems of pure graphene coating are presented.
- Physical and chemical dispersion methods of graphene are introduced.
- Anti-corrosion mechanism of graphene composite coatings is summarized.
- Future development directions for graphene anti-corrosive coatings are proposed.