

Graphene Composite Anticorrosive Coatings: Research Progress in Mechanism, Dispersion and Alignment

Zhirui Wu

University of Shanghai for Science and Technology, Shanghai 200093, China

*wzr1207@126.com

Abstract

As a two-dimensional nanomaterial, graphene has many excellent properties and is widely used in polymer composite coatings. In recent years, the field of graphene composite anticorrosive coatings is booming. This paper first briefly introduces the way to improve the dispersion of graphene in organic polymers. Secondly, the anti-corrosion mechanism of graphene in composite coatings and the optimization of graphene composite coatings by directional arrangement are reviewed in detail. The anti-corrosion mechanism is based on barrier enhancement and cathodic protection to improve coating performance, and the effects of different methods of directional arrangement on coating performance are described. Finally, the existing problems and development direction of graphene composite anticorrosive coatings are prospected.

Keywords

Graphene; Anticorrosion Mechanism; Composite Coating; Directional Arrangement; Dispersed.

1. Introduction

Graphene composite anti-corrosion coatings are widely used to protect metals against oxidation and corrosion because of its excellent properties such as high mechanical strength, great surface area and extremely compact mesh structure[1].

The research of graphene anticorrosive coating is divided into pure graphene coating and composite coating. Pure graphene coatings are relatively expensive to prepare, difficult to produce on a large scale industrially, and can aggravate metal corrosion when the coating is damaged[2]. Therefore, more and more researchers are focusing on the development of graphene composite anticorrosive coatings. Compared with pure graphene coatings, composite coatings not only consider the excellent chemical stability and fast electrical conductivity of graphene, but also the excellent properties of graphene electromagnetic shielding[3], mechanical property enhancement[4], weathering resistance[5] and self-cleaning ability[6], as a way to improve the comprehensive anticorrosion performance of the coatings. At present, many scholars have published a review article in this field. For example, Zhu Jiankang et al.[7] summarized the structural characteristics of graphene and the problem of micro-galvanic corrosion in the application of anticorrosive coatings, and summarized various solutions such as surface insulation of graphene, development of graphene zinc-rich coatings and design of graphene-based self-healing functional coatings. Li Shuang[8] and other scholars deeply analyzed the characteristics, functions and preparation techniques of graphene, elaborated its role in the field of anticorrosion, and summarized the latest development of various graphene anticorrosive coatings, which provided an important reference for practical applications. Ding Jiantao et al.[9] reviewed two main methods to improve the dispersion of graphene, chemical modification and physical dispersion, and focused on the analysis of two methods for graphene and oxide. However,

the existing review articles on graphene composite coatings lack a comprehensive summary of the methods for inducing the directional alignment of graphene and also a summary of the optimization of graphene composite coatings.

Based on the existing review literature on the dispersion and mechanism of graphene composite anticorrosive coatings, this paper summarizes in detail the anticorrosive mechanism of graphene composite anticorrosive coatings, and theoretically complements and improves the enhancement of cathodic protection, and elaborates the way and role of graphene-induced parallel arrangement, which are of great significance to the development of anticorrosive graphene composite coatings.

2. Anticorrosion Mechanism of Graphene Composite Coating

Graphene and its derivatives have great potential in the field of anticorrosion due to their large specific surface area, strong molecular impermeability, excellent mechanical properties and low chemical reactivity. Graphene composite coatings can effectively protect metal substrates and retard corrosion, and the basic protection mechanisms are barrier protection and cathodic protection. In addition, functionalized graphene has good protective properties for anticorrosive coatings. In this section, I will explain the anticorrosion mechanism of graphene composite coating and explain the improvement of its anticorrosion performance according to the various functional characteristics of graphene composite coating.

Table 1. Summary of graphene composite anticorrosive coating mechanism[10-15]

Anticorrosion mechanism	Basis	Coating composition	Film forming mode	Anticorrosion test	Reference
Barrier enhancement	Copper plate	FG,PVB	Dip-coating	EIS	[10]
	Zinc plate	PVP-rGO, Epoxy resin	Casting process	TAFEL	[11]
	Steel plate	PI-GO,PU	Dip-coating	EIS	[12]
Cathodic protection	Q235 low carbon steel	rGO,Epoxy zinc rich resin	Rod coating method	EIS	[13]
	Q235 low carbon steel	PANI-Gr, Epoxy zinc rich resin	Automatic coating method	OCP, EIS	[14]
	DH32 steel	SDBS-Gr, Epoxy resin	Spraying method	OCP, EIS	[15]

2.1 The Enhanced Barrier Effect of Graphene

When a pure polymer coating is used, the corrosive medium will penetrate into the substrate with the coating. Once the corrosive medium contacts the metal surface, corrosion reaction will occur.

Graphene consists of sp²-hybridized carbon atoms with a high electron density on the aromatic ring that blocks all molecules [16], as shown in Figure 1. Therefore, the specific structure of graphene achieves its impermeability. The permeability of graphene can significantly improve the performance of the coating, it can effectively extend the permeation path and thus provide effective shielding protection to the coating, which can significantly enhance its corrosion resistance and extend its service life.

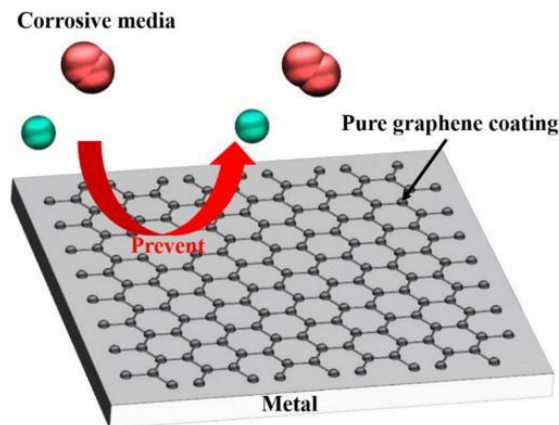


Figure 1. Graphene acts as an anti-corrosion barrier to prevent oxidation [16]

Zhu et al.[17] synthesized a water-dispersible graphene and used it as a nano-reinforced pigment in waterborne acrylic modified alkyd resin coatings. The high dispersion and high aspect ratio of graphene significantly enhance the barrier effect of the composite coating on gas and water, thereby improving the corrosion resistance of the composite coating. The modified graphene can significantly improve the dispersion of graphene in the polymer coating and has better barrier effect. Zhang et al. uniformly dispersed graphene nanosheets into epoxy resin by in-situ polymerization ; adding 0.7 wt% graphene to the composite coating can significantly improve its corrosion resistance. The electrochemical behavior of the composite coating on the metal substrate was measured by electrochemical impedance spectroscopy. The results show that the corrosion current (I_{corr}) of graphene composite epoxy coating is $0.18 \mu\text{A}/\text{cm}^2$, which is 4 times lower than that of pure epoxy coating. This is because the high aspect ratio of graphene extends the diffusion path of corrosive particles and plays an effective anti-corrosion role.

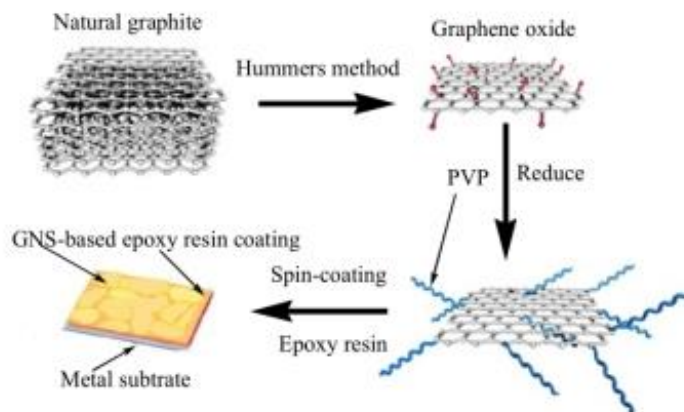


Figure 2. Synthesis process of graphene nanosheet epoxy resin coating [11]

The concentration of modified graphene will significantly affect the shielding effect of the coating. A certain amount of functionalized fossil graphene can be uniformly dispersed in the coating matrix, but too much addition will lead to the accumulation and distribution of graphene in the coating, resulting in voids and reducing the corrosion resistance of the coating. Liu et al.[10] found that adding a small amount of functional fossil graphene to the epoxy resin matrix will cause rough surfaces and some cracks. As the concentration of fossil graphene increases (resulting in rough surface, as shown in Figure 2c), fossil graphene exhibits good dispersion and compatibility in the epoxy matrix without aggregation. When the concentration increases to 1.0 wt%(Figure 2e), aggregation occurs between the matrix and the nano-filler, and the binding effect is poor, the shielding effect of the coating is

weakened, and the corrosion resistance is reduced. In addition, the multilayer graphene coating has better oxidation resistance than the monolayer graphene coating. The overlap of multilayer graphene coatings produces steric hindrance, which effectively prevents the diffusion of corrosive media in the vertical direction.

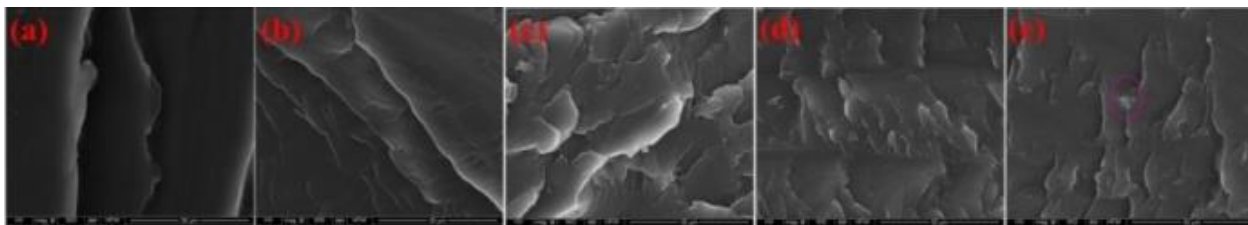


Figure 3. (a) Cross-sectional morphology of pure EP and EP composite coatings containing (b) 0.25 wt% FG, (c) 0.5 wt% FG, (d) 0.75 wt% FG, (e) 1.0 wt % FG [10]

In addition, graphene can also achieve excellent corrosion resistance by enhancing the resistance of the coating to corrosive media. In neutral and alkaline environments, the hydroxyl and carboxyl groups of the edge functional groups of graphene oxide produce negative charges due to deprotonation, as shown in Figure 4. The ionic resistance of the coating is affected by the negatively charged GO sheet layer, which prevents the diffusion of OH⁻ and Cl⁻ anions into the coating and enhances the corrosion resistance of the coating. Silanized graphene oxide also has this function [18]. The silane groups on the hydrolyzed functional graphene in the polymer matrix can prevent water from penetrating the epoxy coating. Silanization enhances the barrier effect of the coating and significantly improves the corrosion resistance of the composite coating.

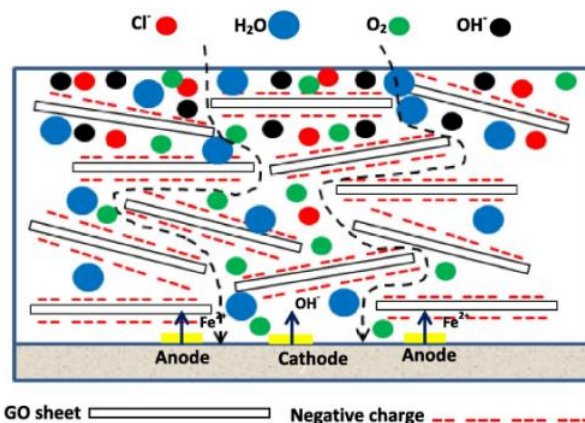


Figure 4. Anticorrosion mechanism of PU coating containing PI-GO nanosheets in 3.5 wt% NaCl solution [12]

2.2 Cathodic Protection of Graphene Composite Anticorrosive Coating

In cathodic protection based anticorrosion coatings, electrochemical protection is usually generated between the added active metals (such as Zn and Al) and the relatively electrochemically inert metal matrix. Zinc-rich coating is the most widely used primer. The content of zinc powder in the coating can be as high as 80-90 wt%. However, a large amount of Zn will increase the porosity of zinc-rich coating and weaken the barrier effect of zinc-rich coating. Therefore, the utilization rate of Zn particles in pure zinc-rich coating is very low. The addition of graphene as a conductive material can reduce the Zn content. Graphene as a conductive channel can promote the electrical coupling effect between the external Zn and the metal matrix, thereby further improving the cathodic protection effect of the zinc-rich coating.

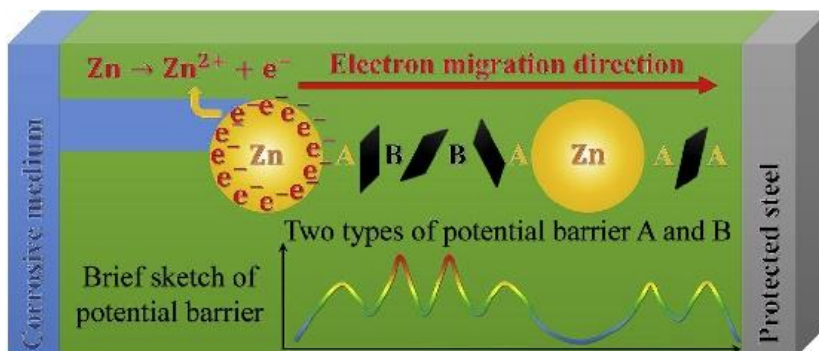


Figure 5. In zinc-rich coatings, the electrons lost due to the zinc sacrificial anode need to pass through two kinds of barriers during the conduction process : (A) metal-graphene barrier and (B) graphene-graphene barrier[19]

From the microscopic point of view, the migration of electrons in the zinc-rich coating is an important factor affecting the cathodic protection performance. Although there is no direct contact between the fillers due to the encapsulation resin, the electrons lost by zinc oxidation migrate to the surface of the steel substrate, thereby reducing dissolved oxygen. Therefore, in the process of transferring electrons lost from the Zn sacrificial anode to the protected metal, the barrier formed by the resin polymer must be passed. As shown in Figure 5, Ding et al.[19] analyzed the modification mechanism of graphene on zinc-rich coatings in detail from the perspective of electron migration and barrier effect, and established relevant physical models and mathematical equations. He divided the barrier into two types according to the type of material on both sides of the barrier : metal-graphene and graphene-graphene.

$$\eta = \frac{3M_{Zn}}{2q_e N_A \rho_{Zn} \pi R^3} f^l(\vec{E})_{|\vec{E}|=E_b} \quad (1)$$

$$D = \frac{\cos^2 \phi}{1 + \sin^2 \phi \cos^2 \left(a \sqrt{\left(\frac{E - U_e}{h_{vF}} \right) - \frac{E^2}{v_F^2} \cdot \frac{\tan^2 \phi}{1 + \tan^2 \phi}} \right)} \quad (2)$$

The analysis of the physical model and the mathematical equation (1) (2) shows that the $1/\eta$ change of the metal-graphene barrier is more obvious than the D change of the graphene-graphene barrier, so the electrons are easier to pass through the latter. This shows that graphene reduces the difficulty of electron transfer between metals and promotes the cathodic protection of zinc to steel, which is the microscopic explanation of graphene promoting charge transfer and enhancing cathodic protection of zinc-rich coatings.

As mentioned above, the conductivity of graphene can improve the cathodic protection performance of the coating, but too high conductivity will lead to galvanic corrosion between graphene and metal substrate. Due to the high defect density of graphene, the corrosive medium can more easily penetrate into the interface between graphene and metal matrix, which leads to the occurrence of galvanic corrosion, which accelerates the corrosion of anode metal, and also weakens the bonding force between graphene and metal, resulting in the degradation of metal and the failure of coating protection. Sun et al.[20] found that the conductivity of graphene in composite coatings is mainly affected by the degree of functionalization of graphene. Excessive covalent functionalization reduces the conductivity of graphene, thereby inhibiting its corrosion-promoting activity. From a microscopic point of view, the difference in oxygen content on graphene sheets greatly affects the interfacial

interaction of hydrogen bonds, which in turn affects the conductive network of graphene. These results indicate that determining the degree of functionalization is important for the functional application of modified graphene in coatings, and also promotes the development of high-performance graphene-reinforced polymer anticorrosive coatings.

3. Optimization of Graphene on Organic Anticorrosive Coating

3.1 Improve the Dispersion of Graphene

Table 2. Summary of dispersion improvement methods of graphene and its derivatives[11,21-35]

Dispersion method	Modified materials		Modification group	Reference
Mechanical dispersion	/		/	[21]
Wet transfer dispersion	/		/	[22]
Chemical covalent modification	Small organic molecule	Silane coupling agent, titanate coupling agent	-OH, -COOH, epoxy group	[23]
	Organic polymer	Polyaniline, polyvinylpyrrolidone, polyisocyanate	-OH, -COOH, epoxy group	[11,24-25]
	Inorganic nanoparticles	SiO ₂ , TiO ₂	-OH, -COOH, epoxy group	[26-27]
Noncovalent physical adsorption	Electrostatic adsorption	Al ₂ O ₃ , sodium polyacrylate	-OH, -COOH, epoxy group	[28-29]
	Electron orbital conjugation	Polydibutylalanine, pentatetraenoic acid	Six-membered carbon ring	[30-31]
	Hydrogen bond	Polypyrrole, adriamycin hydrochloride	-OH, -COOH	[32-33]
In-situ polymerization	Polyimide, polyaniline		Six-membered carbon ring, -OH, -COOH	[34-35]

The main anti-corrosion mechanism of graphene composite coating is the physical barrier provided by uniformly dispersed graphene sheets. Therefore, the research of graphene dispersion technology has become a hot topic. The dispersion technology of graphene has been widely studied and many good results have been achieved, so here is only a brief introduction.

Unmodified dispersions are usually achieved by simple mechanical dispersion, such as stirring, ultrasonic and other physical methods. However, these methods are only applicable to GO, and it is still difficult to achieve satisfactory compatibility between reduced graphene and polymer matrix because the former lacks active groups on the surface. Through wet transfer dispersion technology, graphene can be effectively extracted from water, extracted and evaporated, and finally transferred to resin. This technology is very similar to mechanical dispersion technology. This method is simple and can obtain good dispersion. Both methods use the principle of similar miscibility of materials, but these two methods are not commonly used.

In order to improve the dispersion efficiency of graphene in polymers, chemical covalent modification or non-covalent physical adsorption has been widely used to improve the compatibility between graphene and polymers. Chemical covalently modified groups can be divided into three types : organic small molecules (such as silane coupling agents, titanate coupling agents), organic polymers (such as polyvinylpyrrolidone, aniline trimer, polyaniline (PANI), polyisocyanate, and polyvinyl alcohol (PVA)) and inorganic nano-oxides (such as nano-silica, titanium dioxide and alumina). The functional groups on the surface of graphene can be linked to the polymer by forming chemical bonds with some groups in the polymer to prevent agglomeration. However, the problem of chemical covalent modification is that covalent bond cleavage or ring-opening reaction often occurs, resulting in the destruction of the excellent barrier effect of graphene structure, which makes corrosive substances such as water, oxygen and chloride ion penetrate. However, the noncovalent physical dispersion method does not have this problem.

3.2 Graphene Directional Arrangement

From the previous section on corrosion protection mechanisms, it is clear that the corrosion resistance of graphene-based polymer composites shows a positive correlation with their barrier properties. A simple model has been proposed by some researchers to study the barrier properties of polymer composites with laminate materials [36].

$$P = P_0 \cdot \frac{(1-\varphi)}{1 + \frac{\alpha}{3N} \cdot \left(S' + \frac{1}{2}\right) \cdot \varphi} \quad (3)$$

Among them, P is the permeability coefficient of graphene-based composites, P0 is the permeability of penetrant in pure polymer, S' is the orientation parameter of graphene nanosheets, φ is the volume fraction of graphene, α is the ratio of graphene nanosheets, and N is the stacking degree of highly loaded graphene.

The barrier effect of composites can be predicted from Equation (1) and is related to the orientation and dispersion of graphene in polymers. Therefore, in the following sections we focus on the progress of graphene orientation in polymer and dispersion in anticorrosion materials.

Based on the above equations, it is clear that the orientation of graphene nanosheets in the polymer matrix significantly affects the barrier properties of the composites. As shown in Figure 6, three orientations are considered for graphene nanosheets incorporated in polymer substrates, including orientation parallel to the substrate ($S'=1$), orientation perpendicular to the substrate ($S'=-1/2$), and random orientation ($S'=0$). When $S'=-1/2$, the incorporated graphene cannot block the diffusion of the corrosive medium. In contrast, the barrier properties of the composite can be enhanced by incorporating ($S'=1$) or ($S'=0$) oriented graphene. Graphene that is completely parallel to the substrate maximizes the curvature of the diffusion path, which can significantly improve the barrier performance of the composite.

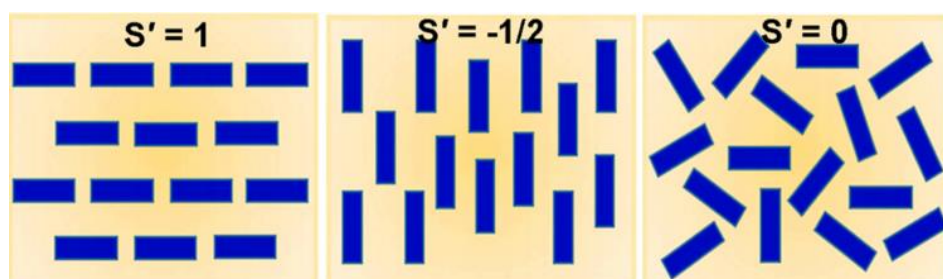


Figure 6. Orientation of graphene sheets in polymer substrates [36]

The physical barrier performance realized by uniform distribution of graphene is the main anti-corrosion mechanism of graphene composite coatings. Well-dispersed graphene increases the curvature of the corrosive medium through the penetration path of the coating and improves its barrier effect.

The electric field induction method refers to the method of using the external electric field to align the graphene in the composite material. Under the action of the applied electric field, the conductive material in the composite material produces a dipole moment due to polarization. The dipole moment is the moment at which the particles deflect. Under the action of the moment and the internal force of the material, the graphene sheet deflects and realizes the directional arrangement of the graphene sheet. Wu et al.[37] prepared oriented graphene nanosheets in resin polymer by AC electric field induction method, and proposed the physical mechanism of GNPs oriented arrangement. As shown in Figure 7, in the sinusoidal alternating field, it is easy to induce polarization and obtain the dipole moment of GNPs. Due to the shape anisotropy of GNPs, the dipole moments parallel to GNPs are much larger than those perpendicular to them, resulting in the reversal of GNPs and then alignment along the direction parallel to the electric field. The AC electric field is more likely to induce graphene orientation than the DC electric field, because the electrophoresis phenomenon is more likely to occur, which promotes the aggregation of graphene near the electrode, thereby achieving better self-alignment and parallel arrangement in the coating plane.

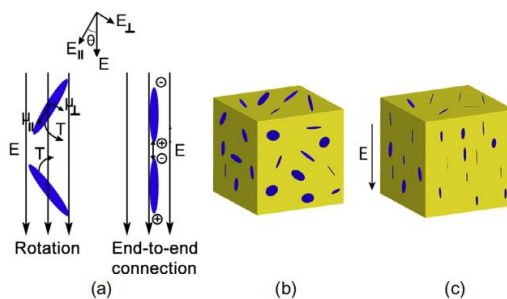


Figure 7. The arrangement mechanism of AC electric field on GNPs : (a) end-to-end connection of rotating polarized GNPs ; (b) Initial random orientation in epoxy resin ; (c) GNPs oriented along the electric field direction in epoxy resin [37]

In addition to the electric field, the magnetic field can also induce the directional arrangement of graphene. External magnetic field induction mainly refers to the modification of graphene to load magnetic particles on the surface of graphene, and then under the action of magnetic field, induced dipole moment is generated, and graphene is arranged along the direction of magnetic field under the action of dipole moment. The magnetism of graphene is determined by its special structure and characteristics. Therefore, in order to make graphene maintain its original direction in the external magnetic field, it must be functionalized to make it magnetic. Therefore, the surface of graphene can be covered with materials such as Fe₃O₄ or Fe₂O₃.

In the study of magnetic field-induced alignment of graphene, Renteria et al.[38] used Fe₃O₄ nanoparticles to functionalize graphene (Figure 10), and achieved the alignment of graphene in the composite at a magnetic field intensity of about 1.2 T. However, the directional arrangement of graphene induced by strong magnetic field requires high cost, which is not conducive to industrial application. As researchers continue to explore, Liu et al.[39] obtained magnetic graphene by using the interaction between chemical bonds, and achieved directional orientation in epoxy resin under the action of an external weak magnetic field (0.04 T). After the graphene is aligned, the properties of the composites are significantly improved.

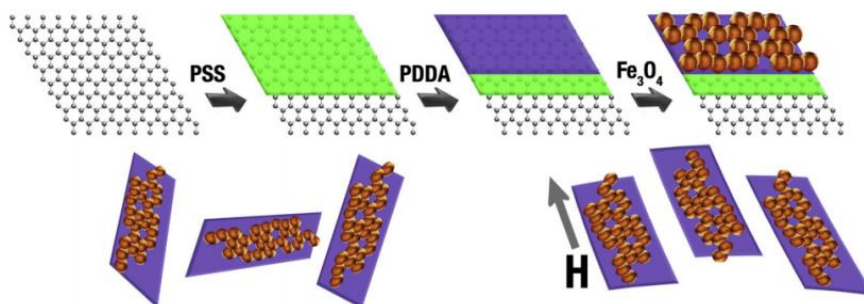


Figure 8. Fe₃O₄ nanoparticles functionalized graphene was aligned under magnetic field [38]

3.2.1 Sub-section Headings

In addition to the above-mentioned use of field-induced alignment of graphene, people have also explored various methods. Notable methods include layer-by-layer self-assembly, filtration-induced self-assembly, and shear force induction.

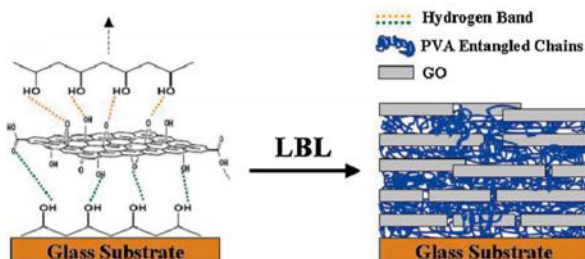


Figure 9. The principle of directional arrangement of graphene by layer-by-layer self-assembly method [40]

Layer-by-layer self-assembly is an effective method for preparing multilayer composite films or layered nanomaterials from bottom to top based on interaction forces (hydrogen bonds, van der Waals forces, electrostatic interactions, etc.). GO is usually used for self-assembly or graphene surface functionalization to make graphene self-assembly. Zhao et al.[40] successfully prepared ultra-thin multilayer PVA/GO nanofilms by bottom-up layer-by-layer assembly of polyvinyl alcohol (PVA) and exfoliated GO. According to Figure 9, the hydrogen bond interaction between the oxygen-containing functional groups of the GO layer and the hydroxyl groups on the PVA chain makes the GO layer have to extend toward the substrate, and these functional groups are tightly bonded together to finally achieve the precise positioning of the GO layer. The multilayer graphene anti-corrosion film prepared by layer-by-layer self-assembly cyclic impregnation method significantly improved the mechanical properties of the composite, the elastic modulus increased by 98.7 %, and the hardness increased by 240.4 %.

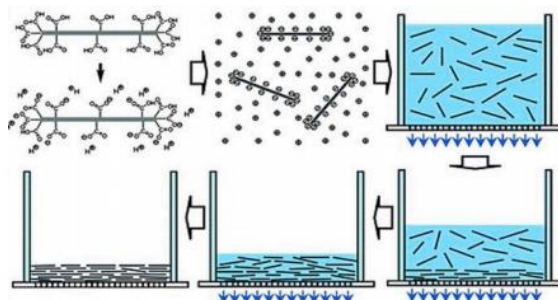


Figure 10. Vacuum filtration induced self-assembly of graphene orientation diagram [41]

Filtration-induced self-assembly is a method to induce the directional arrangement of graphene layers by solvent flow. There are two self-assembly methods for filter-induced oriented graphene composites. One method involves filtering a mixture of graphene and polymer. As shown in Figure 10, when GO is filtered in vacuum, GO nanowires are oriented and arranged horizontally on the filter membrane to form a layer of GO membrane. Another method is to obtain graphene sheets by vacuum filtration of graphene dispersions, and then soak them with resin monomer liquid, so that the liquid penetrates into the gap of graphene sheets, and obtain oriented graphene /resin composites by in-situ polymerization. The functionalized multilayer graphene sheets obtained by this method have excellent electrical conductivity and mechanical properties.

4. Conclusion

Although the corrosion resistance of graphene composite coatings has been extensively studied and some progress has been made, the field is still in the early stage of development, and there is still much work to be done.

(1) In terms of dispersion, the existing research is limited to the dispersion and compatibility between modified graphene and polymer matrix. The interfacial interaction between graphene and other fillers in anticorrosive coatings is still uncertain. It is necessary to study the interface between polymer and metal matrix.

(2) In terms of performance optimization, the degree of functionalization of graphene and the amount of graphene added to the polymer significantly affect the corrosion resistance of the coating. It is necessary to systematically study the effect of the amount and functionalization of graphene on the corrosion resistance, and even study the relationship between them.

(3) In terms of applicability, anticorrosive graphene composite coatings have not yet become mature products and industrial applications. The current research mainly focuses on the short-term corrosion behavior of simple component coatings in laboratory environment. It is necessary to improve the comprehensive evaluation of the performance of anti-corrosion graphene composite coatings and the long-term use evaluation under actual working conditions in various environments.

The research of graphene anticorrosive composite coating shows a good application prospect. The development trend of graphene will be more towards green, high quality, large-scale preparation and multi-functional integration. In the future, industrial resources will be further integrated and will continue to be widely used in industries, new energy and other fields.

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