

Article

Modification of Electrochemical Exfoliation of Graphene Oxide with Dopamine and Tannic to Enhance Anticorrosion Performance of Epoxy Coatings

Suyun Liu, Hu Liu, Ningning Shao and Zhijun Dong * 

Institute of Technology for Marine Civil Engineering, Shenzhen Institute of Information Technology, Shenzhen 518172, China; sylu2021@szit.edu.cn (S.L.); liuhu@szit.edu.cn (H.L.); shaonn@szit.edu.cn (N.S.)

* Correspondence: dongzj@szit.edu.cn

Abstract: Graphene oxide (EGO) was prepared via an electrochemical exfoliation method and modified with dopamine and tannic acid, and it was then incorporated into epoxy resins to enhance their barrier, self-healing and anticorrosion performances. The morphologies, structures and compositions of the HGO (GO prepared via Hummers' method), EGO and MGO (modified EGO) were characterized via SEM, TEM, AFM, Raman spectroscopy and XPS. The protective performances of the epoxy varnish coatings, EGO/epoxy coatings and MGO/epoxy coatings with different contents of MGO were evaluated via EIS measurements, and the role played by MGO on the coating defects was determined via LEIS and salt spray tests on the scratched coatings in a 3.5% NaCl solution. The results show that the dopamine and tannic were successfully grafted onto the EGO surface via π - π interactions and chemical bonding, and that the dispersibility of the MGO in the epoxy resins was facilitated. The epoxy coatings with a 0.1% addition of MGO possessed the best anticorrosion properties ($|Z|_{0.01\text{Hz}} > 10^{10} \Omega \text{ cm}^2$ after 70 days immersion in 3.5% NaCl solution) in comparison to the other coatings due to the "labyrinth effect" formed by the uniformly dispersed MGO. Meanwhile, the grafted tannic acid was released at the coating defects and provided inhibition functionalities for the substrate. As a result, the corrosion of the carbon steel was significantly decreased. This work provides a new perspective on the efficient modification of electrochemically exfoliated GO epoxy coatings for metals by combining the advantages of dopamine and corrosion inhibitors.

Keywords: corrosion protection; carbon steel; graphene; organic coatings; self-healing



Citation: Liu, S.; Liu, H.; Shao, N.; Dong, Z. Modification of Electrochemical Exfoliation of Graphene Oxide with Dopamine and Tannic to Enhance Anticorrosion Performance of Epoxy Coatings. *Coatings* **2023**, *13*, 1809. <https://doi.org/10.3390/coatings13101809>

Academic Editor: Nicolas Mary

Received: 27 September 2023

Revised: 14 October 2023

Accepted: 17 October 2023

Published: 22 October 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Mild steel is commonly used in a wide variety of sectors, such as heavy machinery, transportation and drilling platforms in marine environments, due to its low price, good malleability and formability, and adjustable surface hardness. However, the severe corrosion of mild steel becomes a major concern when the steel is exposed to harsh environments. Approximately USD 900 million in economic losses are caused by corrosion each year. Coatings are the most effective way to protect metals against corrosion among all the protection methods because of their easy-to-prepare, universal and cost-effective characteristics [1–4].

Recently, graphene and its derivatives have been utilized as functional fillers to enhance the shielding effect of organic coatings due to their high chemical stability and strong barrier property [5–7], especially when used in water-based coatings, because graphene oxide (GO) has excellent dispersibility in water solvents with plenty of oxygen-containing functional groups (hydroxy, carboxy and epoxy groups) on its surface and edges [8,9]. However, the anticorrosion performance of water-based coatings is limited because of the presence of hydrophilic hydroxyl, carboxyl and epoxy groups on the resin structure, which allow for the rapid permeation of corrosive media into coatings. Compared with water-based coatings, organic coatings are able to achieve excellent protective effects because of their dense crosslinking structure, but dried GO appears to be gelatinous (including via the

freeze-drying and stove-drying methods), and it is difficult to dissolve or disperse again in organic solvents, leading to aggregations and cracks in the coatings, which could cause a numbers of defects and deteriorate the anticorrosion performance of GO organic coatings [10–12]. Moreover, the commonly used Hummers method to prepare GO consumes a large amount of strong oxidizing chemicals, such as concentrated sulfuric acid and potassium permanganate, and causes a waste of water resources because a great deal of distilled water is needed to clean the prepared GO. Moreover, there is even a risk of explosion.

Very recently, the electrochemical exfoliation preparation of GO (EGO) has received considerable attention because it is environmentally friendly, allows for mass production [13–16] and also accommodates the requirements for large quantities of GO fillers in organic coatings. However, EGO has a low degree of oxidation but high conductivity, leading to poor dispersion stability in organic resins and the “corrosion promotion” effect after long-term service, which still restrict the practical application of graphene composite coatings. Accordingly, attempts have been made to enhance the corrosion protection performance of organic coatings in various ways. Many nanofillers, such as clay nanocomposites [17], SiO₂ [18,19], polyaniline (PANI) [20–22], etc., have been investigated to improve the anticorrosion performance of graphene coatings. However, the complicated fabrication process of water-dispersible graphene and the limitation of its corrosion protection owing to its high electrical conductivity make the effectiveness of it as an additive controversial.

Chemicals with inhibition abilities (phytic acid, tannic acid, imidazole, etc.) [23,24] are able to graft to GO with many oxygenated functional groups (especially prepared via Hummers’ method), which not only improves the dispersibility of GO in organic coatings, but also ensures the self-healing ability of the obtained coatings, improving their barrier property and avoiding the “corrosion promoting effect” of GO, thereby allowing them to achieve a superior anticorrosion performance [25,26]. Nonetheless, how to graft substances with corrosion inhibition abilities onto GO surfaces or edges needs to be addressed. Particularly, dopamine has the characteristics of self-polymerization and can be connected between GO layers owing to π – π interactions as well as covalent bonding, which reduce the interlayer force of the GO and promote its dispersion in organic coatings [27,28]. Furthermore, as a novel covalent linker, dopamine is a perfect candidate to enhance the connection of GO with inhibition substances and organic resins [29,30]. Therefore, there is immense potential in exploiting the synergistic effect between EGO, inhibition chemicals and dopamine in order to realize EGO organic coatings that possess superior anticorrosion properties and inhibition functionalities. Unfortunately, such reports are very scarce in the literature, and there is no relevant method to modify the electrochemical exfoliation of GO. Ultimately, this highly promising method for preparing GO anticorrosion coatings has not achieved widespread application.

In this study, we attempted to design an eco-friendly and cost-effective method to prepare graphene oxide composite coatings with excellent inhibition functionalities and outstanding anticorrosion performances by using an electrochemical exfoliation method to prepare EGO (electrochemically exfoliated GO) and then modifying the EGO with dopamine and tannic acid and incorporating it into epoxy coatings. For comparison, HGO (GO prepared via Hummers’ method) and HGO organic coatings were prepared. The microstructures and chemical compositions of the HGO, EGO and MGO were characterized. The corrosion performances of the as-prepared coatings (epoxy coatings, EGO/epoxy coatings and MGO/epoxy coatings with different additions of MGO) were monitored via electrochemical measurement and the salt spray test. The optimal amount of MGO was determined, and the anticorrosion mechanisms of the coatings were also clarified.

2. Materials and Experiments

In this study, Q235 carbon steel was utilized as the substrate metal and underwent pretreatment based on prior research [12]. HGO was synthesized via the modified Hummers’ method [31,32] and centrifuged to clean the solution with a pH greater than 5. The

preparation process for EGO was carried out in accordance with the report in [13]. Following the electrochemical exfoliation process, the pH of EGO solution was adjusted to above 5 through continuous centrifugation. Subsequently, EGO suspensions were prepared by adding Tris-buffer solution (10 mM, pH = 8.5) via sonication for 30 min. Then, 800 mg of dopamine hydrochloride and tannic acid was added, and this was stirred vigorously for 24 h at room temperature to obtain tannic acid- and dopamine-modified EGO (MGO). After the reaction, the MGO was centrifuged and washed with distilled water several times to remove any unreacted dopamine and tannic acid. The HGO, EGO and MGO solution obtained was subsequently freeze-dried and stored in a brown bottle for the following experiments.

Preparation of the composite coatings: EGO and MGO powders were added to an epoxy/xylene solution and ultrasonicated for 30 min. Polyamide curing agents were then introduced to the mixture, resulting in the preparation of EGO/epoxy and MGO/epoxy coatings. The proportion of epoxy, xylene and curing reagent was 10:5:8. The coatings were applied to the Q235 carbon steel electrode via manual brushing and cured in an oven at 40 °C for 4 h and 60 °C for 20 h. The dry film thickness of the coatings was measured using a hand-held electronic gauge (PosiTector 6000, Defelsko, NY, USA) in accordance with ISO 2808-1997. The dry film thickness of all coatings was maintained at $100 \pm 10 \mu\text{m}$. It is worth noting that EGO/epoxy coatings with a 0.1% EGO content and 0.05 MGO/epoxy, 0.1 MGO/epoxy and 0.2 MGO/epoxy coatings—with MGO contents of 0.05%, 0.1% and 0.2%, respectively—were fabricated. Additionally, epoxy varnish coatings without any GO fillers were prepared to serve as a basis for comparison.

The morphologies and microstructures of the HGO, EGO and MGO were analyzed by utilizing a field-emission scanning electron microscope (FE-SEM, SU8010, HITACHI, Tokyo, Japan) and a transmission electron microscope (TEM, Tecnai G2 F30, FEI, Hillsboro, OR, USA and F200, JEOL, Tokyo, Japan). To determine the thicknesses and heights of HGO, EGO and MGO, an atomic force microscope (AFM, Dimension ICON, Bruker, Luken, Germany) test was conducted. A Raman spectrometer (inVia Raman Microscope, RENISHAW, London, Britain) with a 532 nm laser as an excitation source was utilized to assess the graphitization characteristics of the nanosheets. Additionally, an X-ray photoelectron spectroscope (K-Alpha, Thermo Fisher Scientific, Waltham, MA, USA) was employed to analyze the surface chemical composition of the HGO, EGO and MGO nanosheets acquired.

Electrochemical impedance spectroscopy (EIS), localized EIS measurements (LEIS) and salt spray tests evaluated the protective properties of the coatings. The working electrode consisted of coated Q235 steel and scratched coated Q235 steel, a platinum plate ($2 \text{ cm} \times 2 \text{ cm}$) served as the counter electrode and a saturated calomel electrode (SCE) was the reference electrode. The testing adhered to a standard three-electrode cell. EIS results were taken between 100 kHz and 10 mHz using a sinusoidal voltage with an amplitude of 10 mV at the open-circuit potential (OCP) on a CHI 760E electrochemical workstation (Chenhua, Shanghai, China). A Faraday cage was utilized to minimize external noise during tests, while sealing films were placed on the electrolytic cell opening to prevent water evaporation during immersion in a 3.5% NaCl solution. The solution was changed every 10 days. LEIS (BioLogic, Grenoble, France) was employed to access the localized corrosion behavior of the scratched coatings. Electrochemical signals were collected over a working area measuring $0.3 \times 0.3 \text{ cm}^2$. Salt spray experiments were carried out in compliance with ASTM B117 international standard [33]. To conduct EIS and LEIS measurements, 0.5 cm long artificial scratches were made on the coatings' surfaces. For salt spray tests, a 4 cm long scratch was used. A stereoscopic microscope (VHX, KEYENCE, Osaka, Japan) was employed for capturing images of the coated Q235 steel surfaces after conducting salt spray tests.

3. Results and Discussions

3.1. Morphologies and Dispersibility

The freeze-dried nanosheets and their dispersibility into epoxy/xylene solution were analyzed in this study. Three types of nanosheets, HGO, EGO and MGO, were dispersed in the solution and left to stand for 15 days. The resulting settlement behavior was captured in images of the inverted sample bottles, as shown in Figure 1. The freeze-dried HGO was observed to be gelatinous and difficult to disperse in epoxy/xylene solution. Even with prolonged ultrasonic processing, it still floated on the solution. After 15 days, severe settlement occurred. Preparing HGO/epoxy coatings with excellent barrier performance is challenging because gelatinous HGO can cause significant defects. On the other hand, EGO and MGO are flaky and can be evenly dispersed through ultrasonic processing. It appears that dispersing EGO and MGO should be considered for preparing high-quality coatings. After 15 days of settling, no significant stratification was observed in the EGO and MGO epoxy/xylene solution. However, when the bottle was inverted, a large number of large-sized EGO nanosheets were found at the bottom. Obviously, it is challenging to disperse EGO in epoxy resin, which results in severe aggregation defects in the coatings. No significant settlement of MGO epoxy/xylene solution was observed at the bottom of bottle, and the size of MGO appeared smaller. Dopamine is capable of absorbing onto the surface of EGO, along with the embedding of tannic acid due to self-polymerization and covalent grafting [28]. Thus, the improvement in the corrosion protection performance of the MGO/epoxy coatings may be attributed to the following: (1) Well-dispersed MGO nanosheets can increase the density of the epoxy matrix due to the highly reactive and adhesive nature of dopamine and polydopamine. These compounds contain functional groups such as catechol, amine, and imine, which improve the interfacial interactions between the MGO and epoxy resin. (2) The incorporated MGO nanosheets possess a higher aspect ratio and excellent barrier properties, which effectively block diffusive paths for electrolyte permeation. (3) Tannic acid is released at the coatings' defects and may form Fe-tannic chelates or complexes to hinder the spread of metal corrosion, thereby protecting the underlying substrate from corrosion attack [34,35].

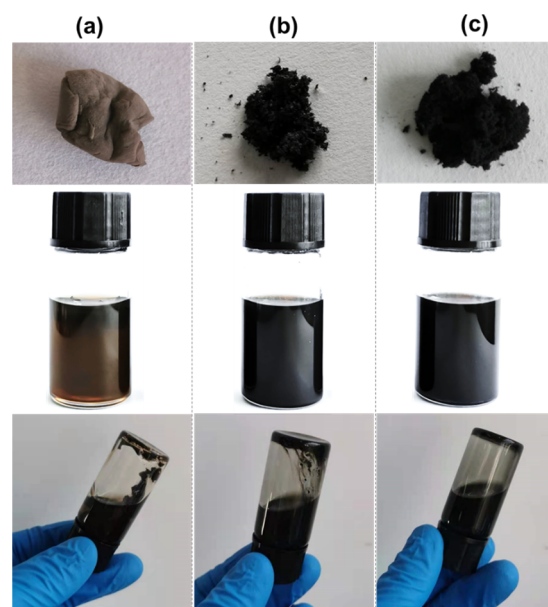


Figure 1. Images of the freeze-dried graphene oxide nanosheets, their dispersibility and inverted sample bottles after 15 days of settlement in epoxy/xylene dispersions of (a) HGO, (b) EGO and (c) MGO.

The microstructures of HGO, EGO and MGO were analyzed using SEM, TEM and AFM measurements, as shown in Figure 2. According to the SEM and TEM data, HGO

possesses a smooth, transparent and thin structure, with fragments interconnected and no sharp borders. This aligns with the gelatinous structure displayed in Figure 1a. The enlarged SEM images and TEM images in Figure 2 confirm the characteristic wrinkled structure of graphene materials, indicating the thinness of HGO. EGO also displays transparency, but seems comparably thicker and smaller than HGO, with observed aggregations. Nevertheless, after modification, MGO nanosheets exhibit a smaller, thinner and more dispersed structure (evident from their wrinkled structure), with the SEM images (Figure 2c) revealing a separation of MGO nanosheets from the large graphene structures. The small size of MGO nanosheets also makes them easy to disperse in epoxy resin and provides superior labyrinth protective effects. AFM findings indicate that the HGO flakes exhibit a lateral size of approximately 3–8 μm with a thickness of less than 1 nm, suggesting fewer layers. EGO exhibits some accumulation phenomena, with a lateral size of the flakes of about 3 μm and a flake thickness of about 10 nm (corresponding to 30 layers of graphene). However, the MGO exhibits a distinct lamellar structure with negligible accumulation, and the thickness of the flakes measures about 1.5 nm (equivalent to fewer than five layers of graphene), indicating a significant improvement in EGO dispersion. The dot-shaped formations observed in AFM images could be a consequence of tannic acid and dopamine adhering to the surface of GO.

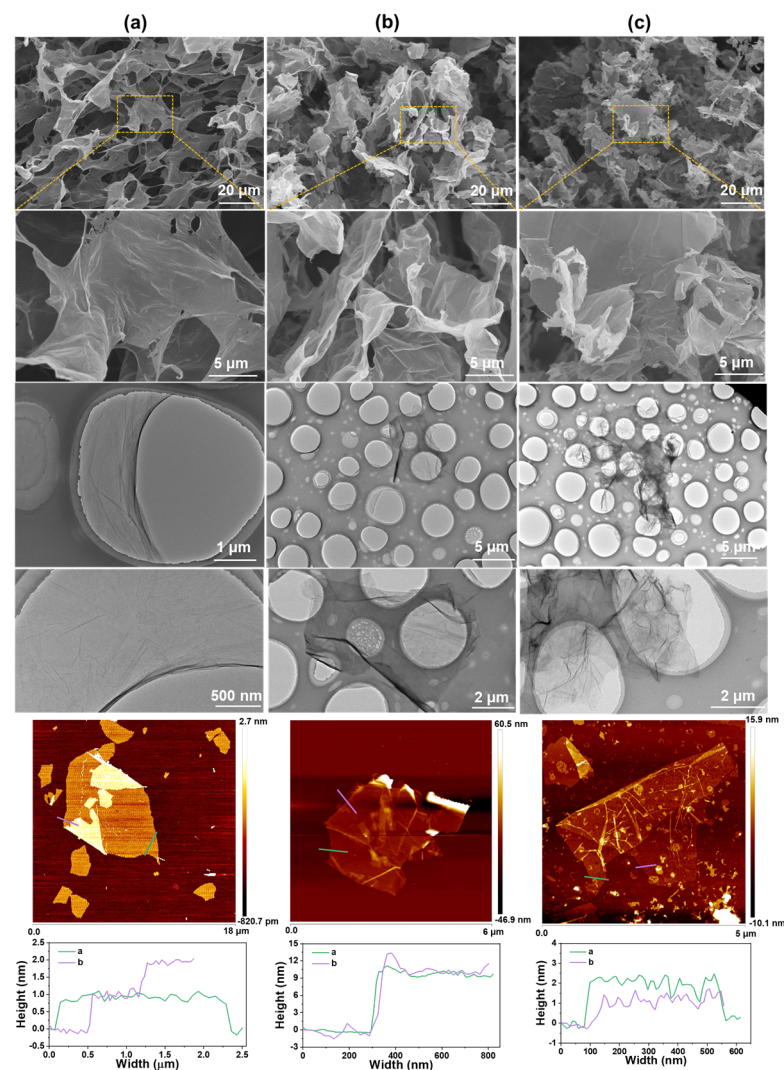


Figure 2. SEM and TEM morphologies at various magnifications, AFM images and the height profiles along the corresponding lines of (a) HGO, (b) EGO and (c) MGO.

3.2. Structure and Composition

Raman spectra were obtained to examine structural variations in the raw graphite, HGO, EGO and MGO nanosheets. The obtained results are displayed in Figure 3a, where D and G bands were observed at 1346 cm^{-1} and 1589 cm^{-1} , indicating the in-plane vibration of sp^2 -bonded carbon and the presence of unorganized carbon [36,37]. Furthermore, the I_D/I_G ratios (peak intensity ratios between the D band and the G band) associated with the ordered crystal structures of carbon atoms in graphene-based materials revealed a substantial increase from 0.04 (graphite) to 0.86 (HGO), 0.41 (EGO) and 1.36 (MGO). The lower I_D/I_G ratio of the EGO nanosheets indicates intact graphitic domains within the structure. This is congruent with the observed greater thickness, as demonstrated by AFM and TEM results. The thicker structure may contribute to higher aggregations and defects within the coatings. MGO demonstrates a higher I_D/I_G ratio of 1.36 in comparison to HGO (0.86) and EGO (0.41), indicating a decrease in sp^2 carbon sites. This is likely due to the π - π interaction and chemical bonding that occur between graphene oxide nanosheets and dopamine/tannic molecules during the modification process. As a result of this modification, excellent dispersion stability may be achieved.

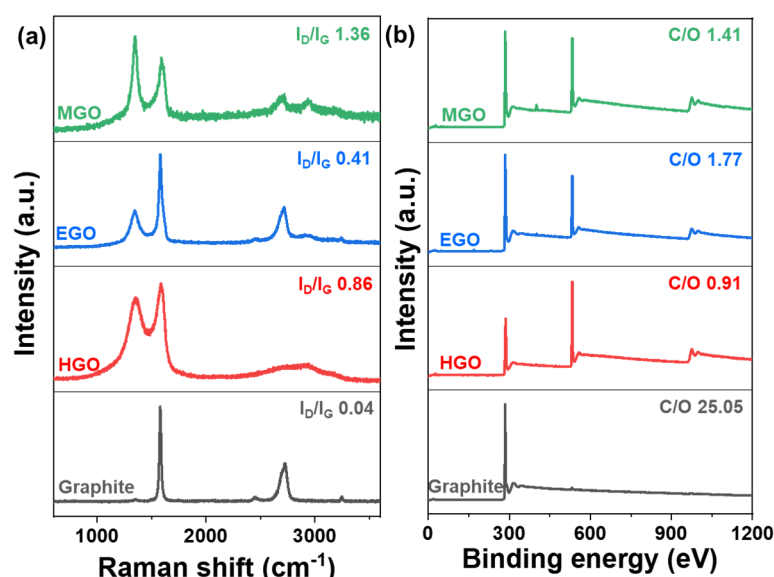


Figure 3. (a) Raman spectra with the I_D/I_G ratio inset and (b) XPS spectra (with C/O ratio inset) of graphite raw materials, HGO, EGO and MGO.

XPS measurements were conducted to further investigate the chemical bonds of the as-prepared HGO, EGO, MGO nanosheets and the raw graphite materials. Figure 3b showcases the outcome of the tests. The O 1s peaks of HGO are strong (indicating a C/O ratio of 0.91) because several oxide groups (carboxyl, hydroxy and epoxide groups) are present in HGO, indicating a partial oxidation of HGO during Hummers' preparation process. Conversely, the O 1s peaks of EGO and graphite feature weaker values of the C/O ratio, which are 4.46 and 25.05, respectively. The degree of oxidation for both is relatively low, suggesting that the incomplete separation of the graphite layers. However, the value of the C/O ratio for MGO is significantly higher than that of EGO, demonstrating that both exfoliation and oxidation processes take place on EGO during its modification with dopamine and tannic acid.

The high-resolution XPS spectra of C 1s and N 1s revealed the detailed chemical bonding of EGO and MGO, as displayed in Figure 4. The spectra displayed only two carbon components, which are C-C and C-O, found at 284.6 eV and 286.6 ± 0.1 eV, respectively. The high-resolution C 1s spectra of MGO indicated four peaks at 284.6 eV (C-C), 285.5 eV (C-N), 286.4 eV (C-O) and 288.5 eV (C=O). Further, the high-resolution N 1s spectra reveal two components, including HN-C=O (399.8 eV) and -N= (401.4 eV) [38,39]. Based on the

above findings, it can be concluded that dopamine/tannic acid modification increases the oxygen-containing functional group, which in turn helps in the interlayer exfoliation of EGO. Moreover, a new chemical bond (C-N) was created through the modification process, along with the π - π interaction effect, ultimately enhancing the dispersion stability of the layers of graphene oxide.

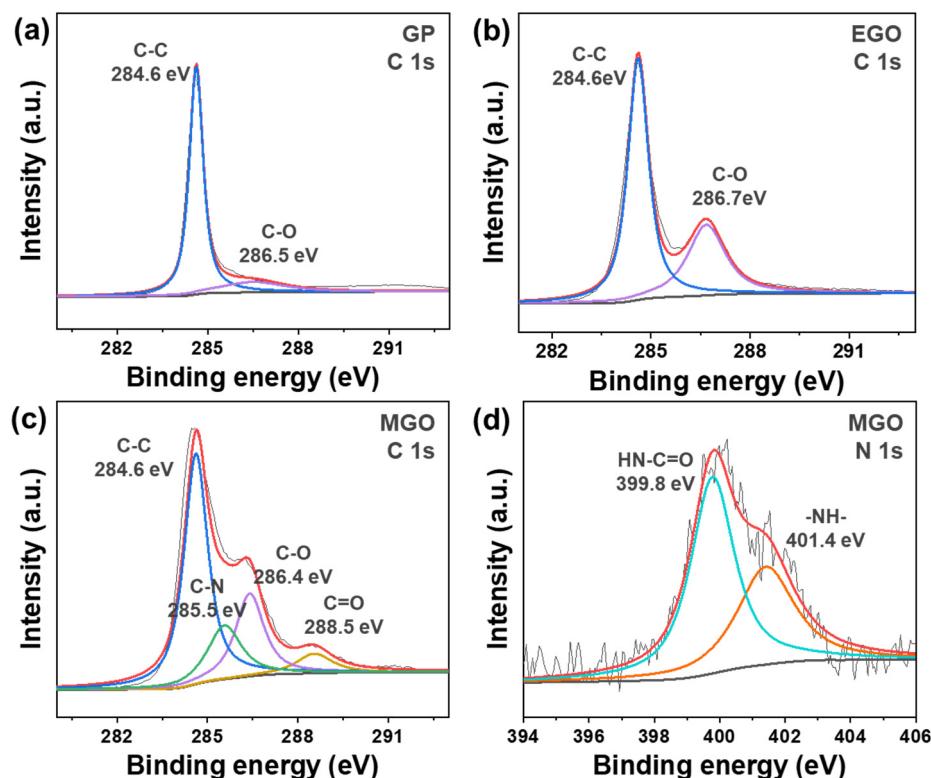


Figure 4. C 1 s spectra of (a) graphite, (b) EGO and (c) MGO, and (d) N 1 s spectra of MGO with deconvoluted peaks.

3.3. Surface Morphologies of Coatings

Figure 5 displays the stereomicroscope morphologies and the partial enlargement of the epoxy varnish coatings, also including the 0.1EGO/epoxy coatings and MGO/epoxy coatings (with MGO content at 0.05%, 0.1% and 0.2%). The transparent epoxy varnish coatings allow all of the dispersed colored fillers to be observed. Many bubbles are visible on the surface of epoxy varnish coatings, which could be a result of rapid solvent evaporation during the curing process. The defects in bubbles create paths for the corrosive media to permeate and accelerate the degradation of epoxy coatings on metal substrates. Following the addition of GO fillers, the quantity of bubbles defects on the surface of coatings diminishes. However, we observed significant aggregations on the surface of EGO/epoxy coatings, largely attributed to the incomplete exfoliation of graphene lamellas and their low dispersibility, as demonstrated by Figures 1 and 2. No apparent bubbles are detected after adding MGO to the mixture, and the MGO fillers are evenly dispersed in the 0.05 MGO/epoxy and 0.1 MGO/epoxy coatings. However, there are some minor aggregations observed in the 0.2 MGO/epoxy coatings as depicted in the partially enlarged image (Figure 5j). The smooth surface of the 0.05 MGO/epoxy and 0.1 MGO/epoxy coatings is precisely due to the modification effects. The presence of dopamine, polydopamine and tannic acid promotes the exfoliation of EGO through both π - π interactions and chemical bonding during the modification process. As a result, the compatibility between MGO and epoxy resin is improved. These uniformly dispersed MGOs can form a “labyrinth shielding” effect, which extends the diffusion path of corrosive media. This leads to a better barrier and protective effect of MGO/epoxy coatings [40,41].

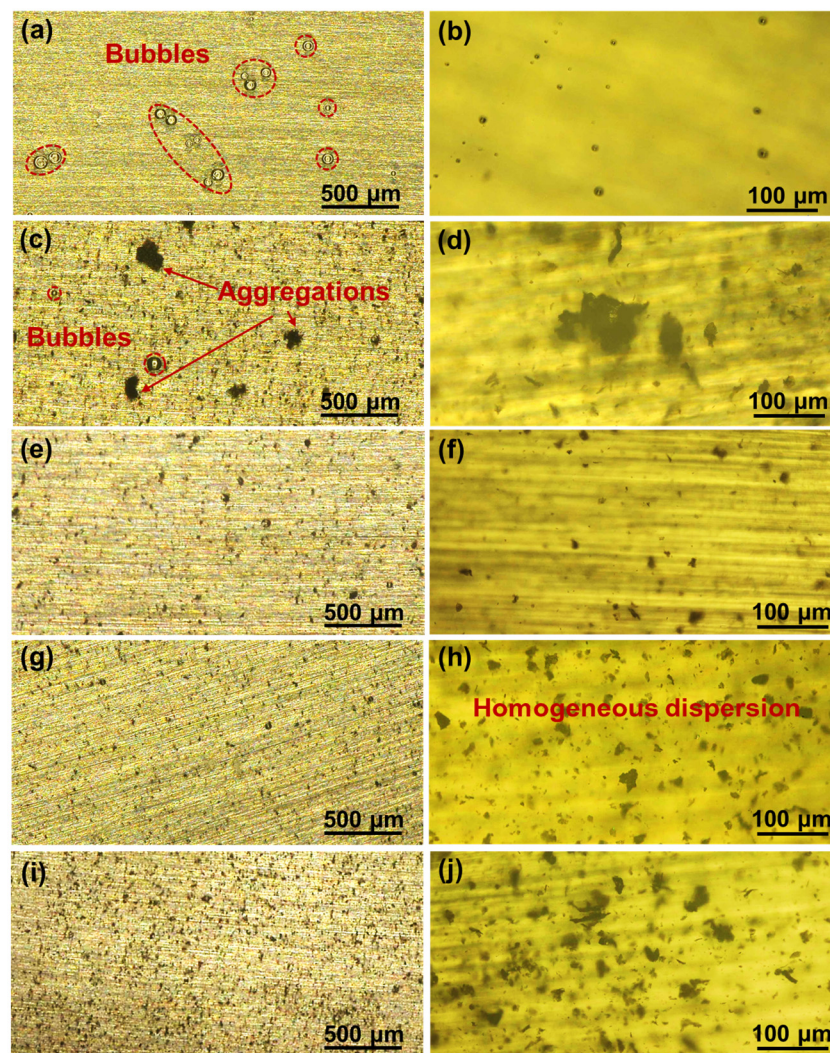


Figure 5. The stereomicroscope morphologies and the partial enlargement of (a,b) epoxy varnish coatings, (c,d) EGO/epoxy coatings with 0.1% EGO addition, (e,f) 0.05 MGO/epoxy coatings, (g,h) 0.1 MGO/epoxy coatings and (i,j) 0.2 MGO/epoxy coatings.

3.4. Anticorrosion Performance

EIS measurements can characterize the alterations in the protective performance of organic coatings during immersion in corrosive media [42–45]. The anticorrosion efficacy of epoxy varnish coatings, EGO/epoxy coatings and different MGO/epoxy coatings were evaluated by submersing them in 3.5% NaCl solution for 25 days, and the Nyquist and Bode plots after 1-day and 25-day immersion are presented in Figure 6a–d. Figure 6e shows a partial enlarged view of Nyquist plots after 25-day immersion to assess the protective performance. In Figure 6f, the impedance modulus of 0.01 Hz of the coatings after 1-day and 25-day immersion is presented. The addition of MGO significantly enhanced the protective ability of the MGO/epoxy coatings in comparison to the epoxy varnish coatings. This was observed in all tested concentrations, including 0.05 MGO/epoxy coatings, 0.1 MGO/epoxy coatings and 0.2 MGO/epoxy coatings (the $|Z|_{0.01\text{Hz}}$ of epoxy coatings increased from $5.87 \times 10^9 \Omega \text{ cm}^2$ to $2.24 \times 10^{10} \Omega \text{ cm}^2$, $3.52 \times 10^{10} \Omega \text{ cm}^2$ and $3.66 \times 10^{10} \Omega \text{ cm}^2$, respectively). The addition of the difficult-to-disperse EGO decreased the anticorrosion performance due to the presence of aggregation defects. The Nyquist plots reveal a capacitive semicircle, whose diameter indicates the barrier property and anticorrosion performance of coatings [43]. The results show that the EGO/epoxy coatings exhibit the lowest semicircle diameter after 1-day and 25-day immersion, implying severe corrosion occurs beneath the coatings. This is attributed to the difficulty in dispersing EGO, which results in aggregations.

However, the barrier properties of the coatings declined slightly with the addition of 0.05% and 0.1% MGO, while a considerable reduction was observed for 0.2 MGO/epoxy coatings after long-term immersion. These findings reveal that the inclusion of a large amount of MGO promotes aggregation formation. Additionally, the $|Z|_{0.01\text{Hz}}$ of 0.05 MGO/epoxy and 0.1 MGO/epoxy coatings remains above $10^{10} \Omega \text{ cm}^2$, even after 25-day immersion in a 3.5% NaCl solution (specifically, $2.16 \times 10^{10} \Omega \text{ cm}^2$ and $2.32 \times 10^{10} \Omega \text{ cm}^2$, respectively). Generally, the impedance modulus at low frequency decreases below $10^8 \Omega \text{ cm}^2$ (it is two orders of magnitude lower compared to our MGO/epoxy coatings) after immersion and causes a loss protection property, again indicating a superior anticorrosion performance of the 0.05 MGO/epoxy and 0.1 MGO/epoxy coatings [44,45]. Conversely, the coatings of epoxy varnish, the EGO/epoxy coatings and the 0.2 MGO/epoxy coating have values of $6.58 \times 10^8 \Omega \text{ cm}^2$, $1.05 \times 10^6 \Omega \text{ cm}^2$ and $6.46 \times 10^7 \Omega \text{ cm}^2$, respectively. To further determine the protective properties of the 0.05 MGO/epoxy and 0.1 MGO/epoxy coatings, longer EIS tests were carried out on the coated system. Figure 7 displays the Nyquist and Bode plots of the 0.05 MGO/epoxy and 0.1 MGO/epoxy coatings after 70-day immersion. It is apparent that the capacitive arcs have a large radius and the low-frequency impedance modulus exceeds $10^{10} \Omega \text{ cm}^2$, indicating their excellent barrier performance, which can be attributed to the uniformly dispersed MGO. However, the addition of 0.1% MGO to the epoxy coatings resulted in a higher impedance modulus at low frequency compared to the coatings containing 0.05 MGO, indicating improved shielding ability. Thus, incorporating 0.1% MGO can significantly enhance the protective property of the epoxy coatings. The anticorrosion performance of coatings improves due to the strong barrier properties of layered materials such as graphene. Graphene can disperse uniformly in the epoxy resin, forming a “labyrinth effect” that extends the diffusion path of corrosive media [46,47]. This facilitated improvements in the coatings’ anticorrosion performance.

To further evaluate the protective efficacy of the coatings and determine the function of EGO/MGO fillers in epoxy coatings, we immersed scratched epoxy varnish coatings, 0.1 EGO/epoxy coatings and 0.1 MGO/epoxy coatings (with a scratch length of 0.5 cm) in a 3.5% NaCl solution for one day. Figure 8 shows the collected Nyquist and Bode plots and fitting data (fitted to the equivalent circuit presented in Figure 9). The Nyquist plots for all coatings exhibit a double capacitive arc, suggesting that the substrate metal corroded because the metal under the coating’s scratch came into contact with the corrosive medium once placed in the solution. The EIS results were fitted using the equivalent circuit depicted in Figure 9a, which includes solution resistance R_s , coating capacitance Q_c , coating resistance R_c , double-layer capacitance Q_{dl} and charge transfer resistance R_{ct} . The values of R_{ct} obtained are depicted in Figure 9b. Generally, a higher R_{ct} value indicates a slower corrosion rate for the substrate metal. However, the corrosion rates for both the epoxy-coated and EGO/epoxy-coated carbon steel clearly increase, as demonstrated by the reduced R_{ct} . Furthermore, the R_{ct} of the EGO/epoxy coating decreases more, which is likely due to the “corrosion promoting effect” of EGO (EGO is conductive and has positive potential compared to metal) [5,6]. The measured R_{ct} of the scratched MGO/epoxy-coated steel increases from $3.035 \times 10^4 \Omega \text{ cm}^2$ to $3.805 \times 10^4 \Omega \text{ cm}^2$ within 1 h to 1 day of immersion. This suggests a decrease in the corrosion of the metal. The superior anticorrosion performance of the MGO/epoxy coating may be attributed to the corrosion inhibition effect of tannic acid. Tannic acid can form dense and insoluble chelate compounds with carbon steel, which effectively counteracts the corrosion-promoting effect caused, as reported by [48,49].

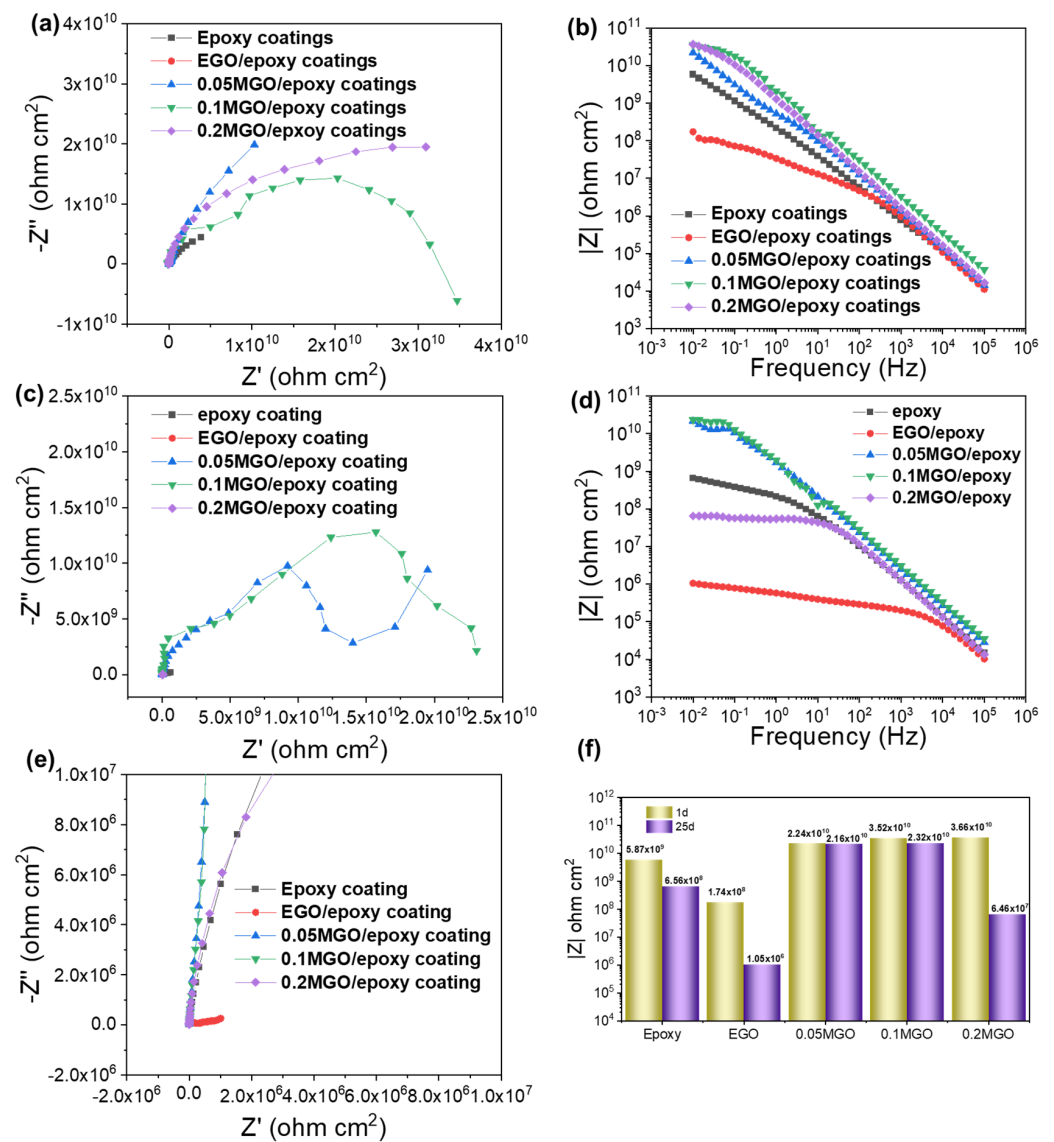


Figure 6. Impedance plots of epoxy varnish coating, EGO/epoxy (0.1% addition of EGO), 0.05 MGO/epoxy, 0.1 MGO/epoxy and 0.2 MGO/epoxy coatings Q235 steel system after (a,b) 1-day and (c,d) 25-day immersion in 3.5% NaCl solution, (e) partial enlargement of (c,f) the obtained impedance modulus at 0.01 Hz.

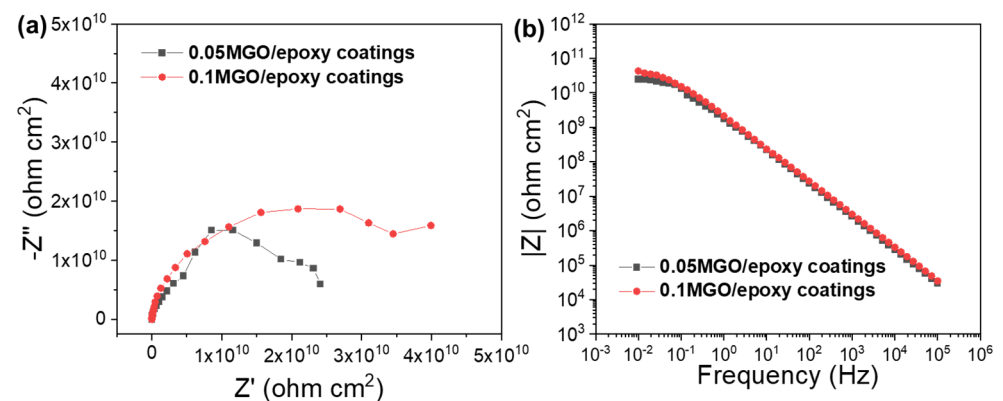


Figure 7. (a) Nyquist and (b) Bode plots of 0.05 MGO/epoxy and 0.1 MGO/epoxy coatings Q235 steel system after 70-day immersion in 3.5% NaCl solution.

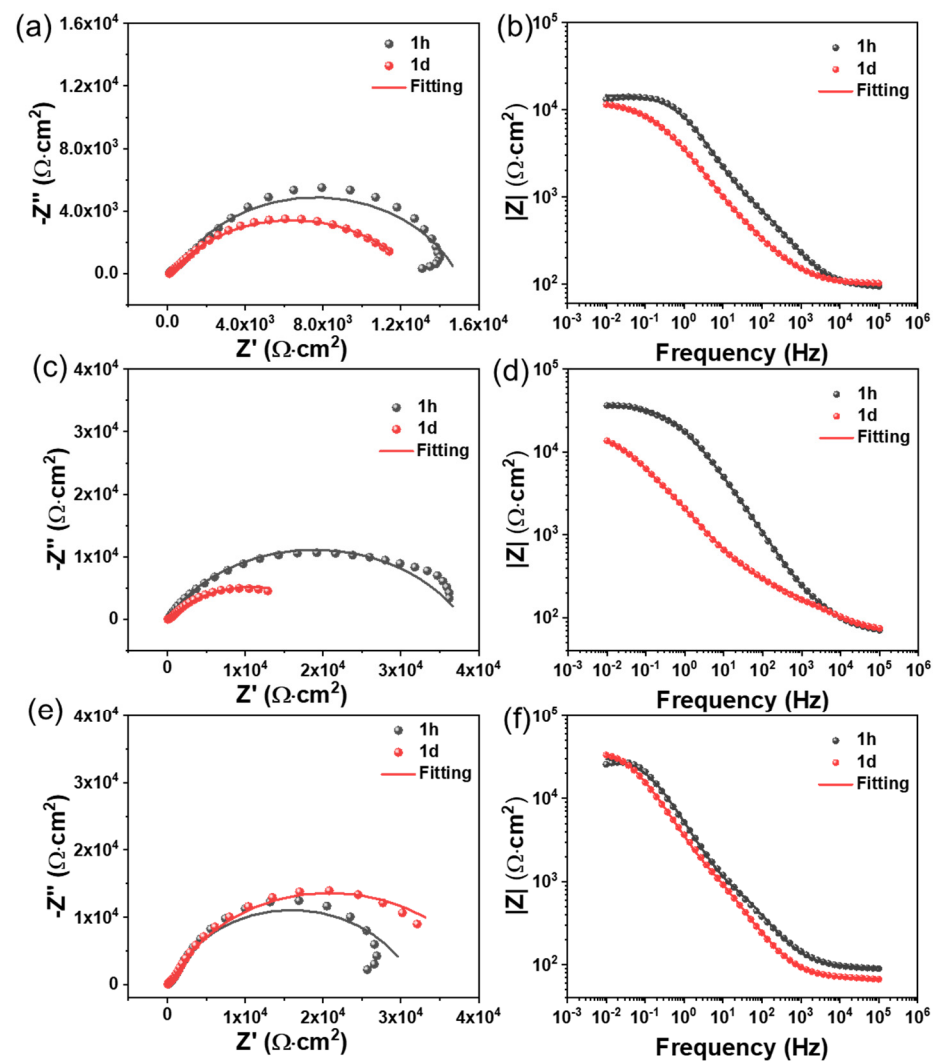


Figure 8. Nyquist and Bode plots with fitting data of the scratched (a,b) epoxy varnish coating, (c,d) 0.1 EGO/epoxy coatings and (e,f) 0.1 MGO/epoxy coatings during 1-day immersion in 3.5% NaCl solution (the scratch size is 0.5 cm in length).

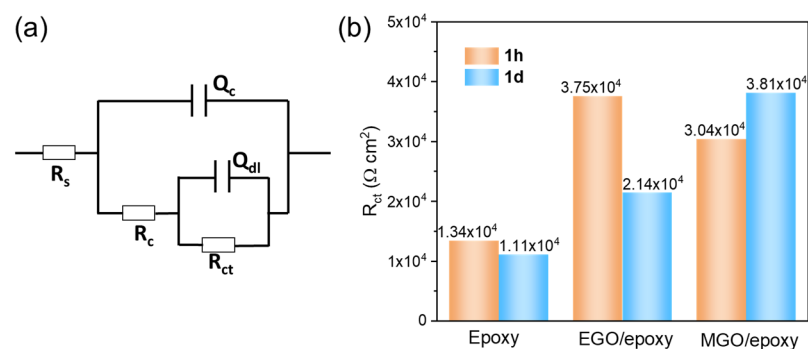


Figure 9. (a) Equivalent circuit of the scratched coated Q235 steel, including solution resistance R_s , coating capacitance Q_c , coating resistance R_c , double-layer capacitance Q_{dl} and charge transfer resistance R_{ct} ; (b) R_{ct} obtained from the EIS fitting results as a function of the immersion time in 3.5% NaCl solution.

To better determine the corrosion protection mechanism of the coatings and clarify the corrosion inhibition effect of MGO, we performed a LEIS test by artificially introducing scratches on their surface [20,39]. Subsequently, the coatings were immersed in 3.5% NaCl

solution for 5 days, and the admittance values of the area ($3 \times 3 \text{ mm}^2$) surrounding the scratches were measured at 1 h, 1 day and 5 days, respectively, as depicted in Figure 10. The tannic acid that was released from the MGO and the coatings reacted with metal substrate when it was placed in the solution. However, tannic acid would eventually diffuse into the solution over time, causing the inhibitory effects to gradually weaken and disappear. Consequently, the LEIS measurements were conducted only for 5 days. The figure displays admittance values that classify corrosion degree into three regions, differentiated by the color of the LEIS images: the whole coating (red area), the coating-scratch interface (green area and adjacent region) and the scratch area (purple area) [20]. The distribution admittance of various coatings within the scratch indicates a considerable shift over the immersion period. Over time, immersion caused the epoxy varnish coating to change from light blue to deep blue, and in the center of the scratch it even transformed to deep purple. Furthermore, the admittance value also underwent significant modification, aligning with the expansion of the artificial scratch area and elevated levels of corrosion, consistent with Figure 10. Around the scratch, the EGO/epoxy coatings also shifted from light blue to dark purple, and the corrosion spread even further throughout the artificial scratch area. The incorporation of EGO nanosheets is believed to harm the corrosion resistance of epoxy coatings because of the “corrosion promotion effect” of conductive graphene materials. On the other hand, the 0.1MGO/epoxy coatings displayed no notable color changes, unlike the epoxy varnish coatings and EGO/epoxy coatings. Furthermore, the admittance value of the 0.1 MGO/epoxy coating’s scratch even slightly rises from 1 h to 1 day before declining from 1 day to 5 days of immersion time. This is attributed to the self-healing ability of tannic acid, which greatly hinders metal corrosion and enhances the coating’s anticorrosion capabilities. These findings align with the preceding EIS analysis.

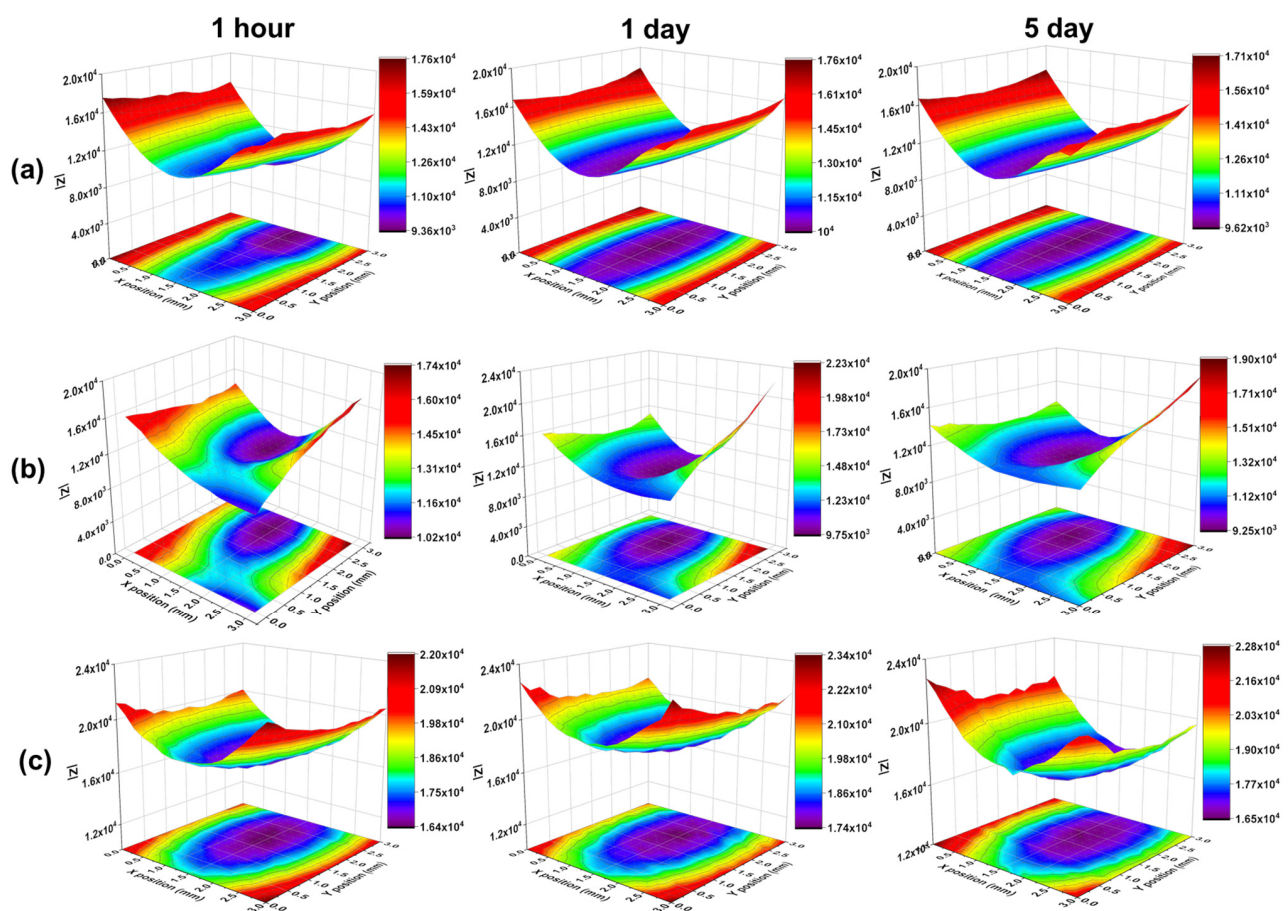


Figure 10. LEIS maps of (a) epoxy varnish coatings, (b) EGO/epoxy coatings and (c) 0.1 MGO/epoxy coatings at different immersion times (1 h, 1 d and 5 d) in 3.5% NaCl solution.

The visual performance of the epoxy, EGO/epoxy and various MGO/epoxy coatings when subjected to salt spray tests for 168 h is shown in Figure 11. Following corrosion tests, substantial amounts of reddish-brown corrosion products, potentially Fe_2O_3 , accumulated around the scratches and permeated deeply within the epoxy coatings and EGO/epoxy coatings. Corrosion pits can form around scratches in EGO/epoxy coatings. This is because the conductive EGO acts as a cathode phase and promotes the corrosion of carbon steel [6,26]. Severe corrosion is also observed on the 0.2 MGO/epoxy coatings, where reddish-brown corrosion products appear in the scratch, and black and reddish corrosion products diffuse inward into the coatings. This may be due to the promotion of corrosion medium diffusion by MGO aggregations at the scratch. The black deposits of corrosion are caused by the reaction between tannic acid and carbon steel. Subsequently, the 0.2 MGO/epoxy coatings also suffered considerable corrosion. However, it is encouraging to note that the addition of 0.05% and 0.1% MGO significantly reduced the corroded area around the coating scratches. The effect was especially pronounced in the corrosion of 0.1 MGO/epoxy coatings, where only a small amount of red and black corrosion products was detected at and around the scratch. Uniformly dispersed MGO has outstanding corrosion inhibition ability and the resulting corrosion products further hinder the corrosion process.

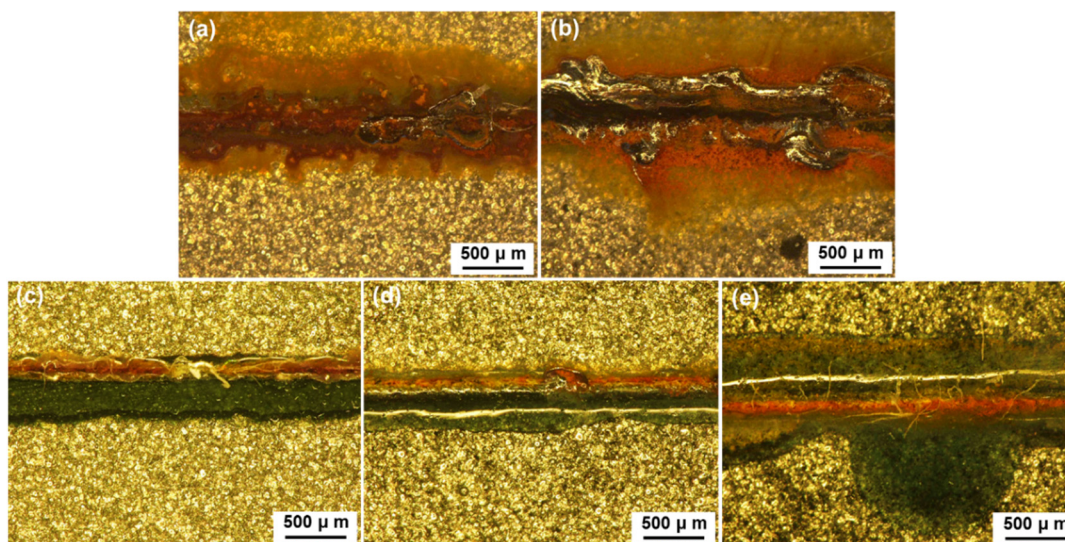


Figure 11. Visual performances of the coatings: (a) epoxy varnish coatings, (b) EGO/epoxy coatings, (c) 0.05 MGO/epoxy, (d) 0.1 MGO/epoxy and (e) 0.2 MGO/epoxy coatings after 168 h exposure to salt spray test, the scratch (5 cm in length) was produced using a sharp blade.

In summary, Figure 12 displays the protection mechanism diagram for the MGO/epoxy coatings. The 3.5% NaCl solution, acting as corrosive medium, penetrates the epoxy coatings and causes significant corrosion of the carbon steel in a relatively short amount of time (as shown on top). After modification and the addition of the well-dispersed MGO (bottom), the corrosive medium is unable to pass directly through MGO and must diffuse in other directions due to the strong barrier properties of graphene materials. This results in an extended and multi-directional diffusion path, which causes the corrosive medium to take a much longer time to diffuse on the substrate surface. As a result, the corrosion of metal is inhibited. This “labyrinth effect” is known to greatly enhance the protective performance of the coatings [40,41]. Moreover, defects in MGO/epoxy coatings allow tannic acid to react with the substrate steel, creating dense and insoluble Fe-tannic complexes/chelates that impede metal corrosion [48,49]. Consequently, MGO/epoxy coatings exhibit significantly enhanced anticorrosion performance.

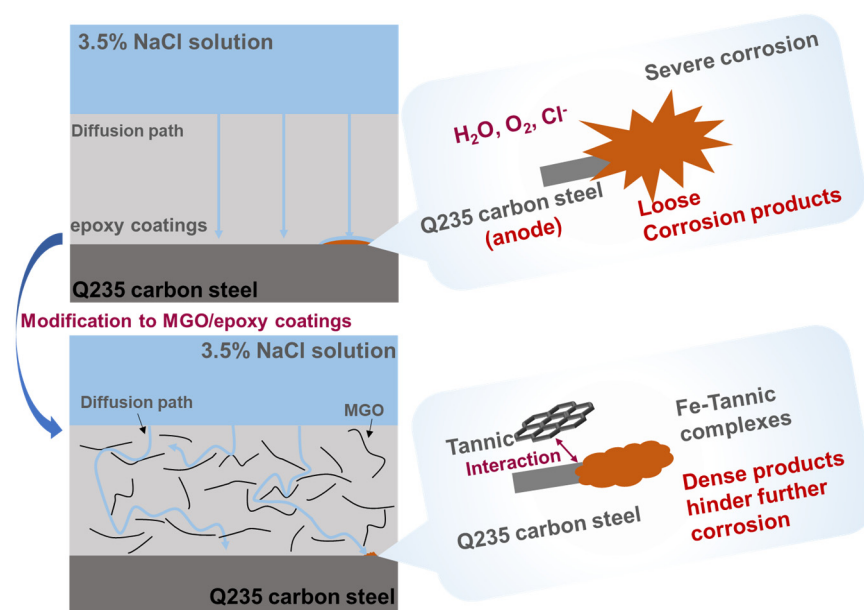


Figure 12. Protection mechanism diagram of the MGO/epoxy coatings displaying the “labyrinth effect” and self-healing inhibition.

4. Conclusions

In this paper, a graphene oxide preparation method using electrochemical exfoliation was employed due to its safety, cost-effectiveness and potential for mass production. EGO was modified using dopamine and tannic acid before being integrated into epoxy coatings for the creation of MGO/epoxy coatings. This study also prepared HGO nanosheets (via Hummers’ method), epoxy vanish coatings and EGO/epoxy coatings for comparison purposes. The thin, transparent and wrinkled appearance of MGO is attributed to the successful connection between dopamine and tannic acid and EGO through π - π interactions and chemical bonds. This significantly enhances the compatibility of MGO with epoxy resin and improves the barrier property of the coatings. EIS tests were conducted on both intact and scratched coatings, with additional salt spray and LEIS tests carried out on the scratched coatings. The results showed that the anticorrosion properties of the EGO/epoxy coatings decreased due to the conductive EGO’s corrosion-promotion effects. Conversely, the protective property of the MGO/epoxy coatings, particularly those with 0.1% MGO, were significantly enhanced thanks to the excellent barrier performance originating from the well-distributed MGO, along with the inhibition functionalities of the released tannic acid. In conclusion, the addition of 0.1% MGO could enhance the barrier and inhibition properties and anticorrosion performance of epoxy coatings.

Author Contributions: Conceptualization, S.L.; methodology, S.L. and H.L.; writing—original draft, S.L. and H.L.; writing—review and editing, S.L.; resources, N.S. and Z.D.; supervision, N.S. and Z.D.; funding acquisition, S.L., H.L., N.S. and Z.D. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Shenzhen Science and Technology Innovation Committee (JCYJ20220817212651001), Guangdong Provincial Department of Education Project (2023KTSCX323), Guangdong Basic and Applied Basic Research Foundation (Nos. 2020A1515110878 and 2022A1515110823) and the National Natural Science Foundation of China (Nos. 51978414 and 52001214).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Rahali, E.; Alves, M.M.; El-Bassi, L.; Bousselmi, L.; de Fátima Montemor, M.; Akrou, H. Enhanced protection of hybrid polyetherimide-ZnO or CuO bilayer composite coatings against mild steel corrosion in chloride media. *Prog. Org. Coat.* **2022**, *163*, 106602. [\[CrossRef\]](#)
- Wang, Y.; You, Z.; Ma, K.; Dai, C.; Wang, D.; Wang, J. Corrosion resistance of a superhydrophobic calcium carbonate coating on magnesium alloy by ultrasonic cavitation-assisted chemical conversion. *Corros. Sci.* **2023**, *211*, 110841. [\[CrossRef\]](#)
- Cui, H.; Tang, F.J.; Li, B.; Lin, Z.B. Microstructure and corrosion resistance of quartz sand-modified enamel-coated steel plates. *Coatings* **2023**, *13*, 1704. [\[CrossRef\]](#)
- Zhang, S.D.; Xu, Y.H.; Liu, L.K.; Lei, Q.D.; Dong, J.L.; Zhang, T. Preparation of Conductive and Corrosion Resistant Phosphate Conversion Coating on AZ91D Magnesium Alloy. *Coatings* **2023**, *13*, 1706. [\[CrossRef\]](#)
- Cui, G.; Bi, Z.; Zhang, R.; Liu, J.; Yu, X.; Li, Z. A comprehensive review on graphene-based anti-corrosive coatings. *Chem. Eng. J.* **2019**, *373*, 104–121. [\[CrossRef\]](#)
- Ding, R.; Chen, S.; Lv, J.; Zhang, W.; Zhao, X.-D.; Liu, J.; Wang, X.; Gui, T.-J.; Li, B.-J.; Tang, Y.-Z.; et al. Study on graphene modified organic anti-corrosion coatings: A comprehensive review. *J. Alloys Compd.* **2019**, *806*, 611–635. [\[CrossRef\]](#)
- Zhang, T.T.; Zhang, Y.K.; Chen, C.; Tian, Y.K.; Wang, Y.L.; Cao, S.Y.; Ma, J. Corrosion-resistant SiO₂-graphene oxide/epoxy coating reinforced by effective electron beam curing. *Prog. Org. Coat.* **2023**, *184*, 107855. [\[CrossRef\]](#)
- Li, H.; Xue, C.; Gao, L.; Wang, X.; Wei, H.; Nan, H.; Wang, G.; Lin, H. “Labyrinthine structure” anticorrosive water-based composite coatings. *Prog. Org. Coat.* **2021**, *150*, 105974. [\[CrossRef\]](#)
- Zhou, X.N.; Huang, H.W.; Zhu, R.; Chen, R.J.; Sheng, X.X.; Xie, D.L.; Mei, Y. Green modification of graphene oxide with phytic acid and its application in anticorrosive water-borne epoxy coatings. *Prog. Org. Coat.* **2020**, *143*, 105601. [\[CrossRef\]](#)
- Zhong, F.; He, Y.; Wang, P.; Chen, C.; Lin, Y.; Wu, Y.; Chen, J. Self-assembled graphene oxide-graphene hybrids for enhancing the corrosion resistance of waterborne epoxy coating. *Appl. Surf. Sci.* **2019**, *488*, 801–812. [\[CrossRef\]](#)
- Pourhashem, S.; Vaezi, M.R.; Rashidi, A.; Bagherzadeh, M.R. Exploring corrosion protection properties of solvent based epoxy-graphene oxide nanocomposite coatings on mild steel. *Corros. Sci.* **2017**, *115*, 78–92. [\[CrossRef\]](#)
- Liu, S.; Wang, X.; Yin, Q.; Xiang, X.; Fu, X.-Z.; Wang, X.-Z.; Luo, J.-L. A facile approach to fabricating graphene/waterborne epoxy coatings with dual functionalities of barrier and corrosion inhibitor. *J. Mater. Sci. Technol.* **2022**, *112*, 263–276. [\[CrossRef\]](#)
- Pei, S.; Wei, Q.; Huang, K.; Cheng, H.-M.; Ren, W. Green synthesis of graphene oxide by seconds timescale water electrolytic oxidation. *Nat. Commun.* **2018**, *9*, 145. [\[CrossRef\]](#)
- Parvez, K.; Wu, Z.-S.; Li, R.; Liu, X.; Graf, R.; Feng, X.; Muellen, K. Exfoliation of Graphite into Graphene in Aqueous Solutions of Inorganic Salts. *J. Am. Chem. Soc.* **2014**, *136*, 6083–6091. [\[CrossRef\]](#)
- Parvez, K.; Li, R.; Puniredd, S.R.; Hernandez, Y.; Hinkel, F.; Wang, S.; Feng, X.; Muellen, K. Electrochemically Exfoliated Graphene as Solution-Processable, Highly Conductive Electrodes for Organic Electronics. *ACS Nano* **2013**, *7*, 3598–3606. [\[CrossRef\]](#) [\[PubMed\]](#)
- Komba, N.; Wei, Q.; Zhang, G.; Rosei, F.; Sun, S. Controlled synthesis of graphene via electrochemical route and its use as efficient metal-free catalyst for oxygen reduction. *Appl. Catal. B-Environ.* **2019**, *243*, 373–380. [\[CrossRef\]](#)
- Atta, A.M.; Ezzat, A.O.; El-Saeed, A.M.; Wahby, M.H.; Abdallah, M.M.S. Superhydrophobic organic and inorganic clay nanocomposites for epoxy steel coatings. *Prog. Org. Coat.* **2020**, *140*, 105502. [\[CrossRef\]](#)
- Haeri, S.Z.; Ramezanzadeh, B.; Asghari, M. A novel fabrication of a high performance SiO₂-graphene oxide (GO) nanohybrids: Characterization of thermal properties of epoxy nanocomposites filled with SiO₂-GO nanohybrids. *J. Colloid. Interf. Sci.* **2017**, *493*, 111–122. [\[CrossRef\]](#)
- Li, W.; Zhang, L.; Zhang, M.; Dou, W.; Zhang, X.; Chen, S. The effects of interfacial water and SiO₂ surface wettability on the adhesion properties of SiO₂ in epoxy nanocomposites. *Appl. Surf. Sci.* **2020**, *502*, 144151. [\[CrossRef\]](#)
- Ye, Y.W.; Yang, D.P.; Zhang, D.W.; Chen, H.; Zhao, H.C.; Li, X.G.; Wang, L.P. POSS-tetraaniline modified graphene for active corrosion protection of epoxy-based organic coating. *Chem. Eng. J.* **2020**, *383*, 123160. [\[CrossRef\]](#)
- Ramezanzadeh, B.; Bahlakeh, G.; Ramezanzadeh, M. Polyaniline-cerium oxide (PANI-CeO₂) coated graphene oxide for enhancement of epoxy coating corrosion protection performance on mild steel. *Corros. Sci.* **2018**, *137*, 111–126. [\[CrossRef\]](#)
- Prabhu, R.; Roopashree, B.; Jeevananda, T.; Rao, S.; Reddy, K.R.; Raghu, A.V. Synthesis and corrosion resistance properties of novel conjugated polymer-Cu₂Cl₄L₃ composites. *Mater. Sci. Energy Technol.* **2021**, *4*, 92–99. [\[CrossRef\]](#)
- Wang, W.; Wang, H.; Zhao, J.; Wang, X.; Xiong, C.; Song, L.; Ding, R.; Han, P.; Li, W. Self-healing performance and corrosion resistance of graphene oxide-mesoporous silicon layer-nanosphere structure coating under marine alternating hydrostatic pressure. *Chem. Eng. J.* **2019**, *361*, 792–804. [\[CrossRef\]](#)
- Feng, L.; Yuan, P. Corrosion protection mechanism of aluminum triphosphate modified by organic acids as a rust converter. *Prog. Org. Coat.* **2020**, *140*, 105508. [\[CrossRef\]](#)
- Du, P.; Wang, J.; Liu, G.; Zhao, H.; Wang, L. Facile synthesis of intelligent nanocomposites as encapsulation for materials protection. *Mater. Chem. Front.* **2019**, *3*, 321–330. [\[CrossRef\]](#)
- Lee, J.; Berman, D. Inhibitor or promoter: Insights on the corrosion evolution in a graphene protected surface. *Carbon* **2018**, *126*, 225–231. [\[CrossRef\]](#)
- Yang, N.; Yang, T.; Wang, W.; Chen, H.; Li, W. Polydopamine modified polyaniline-graphene oxide composite for enhancement of corrosion resistance. *J. Hazard. Mater.* **2019**, *377*, 142–151. [\[CrossRef\]](#)

28. Cui, M.; Ren, S.; Zhao, H.; Xue, Q.; Wang, L. Polydopamine coated graphene oxide for anticorrosive reinforcement of water-borne epoxy coating. *Chem. Eng. J.* **2018**, *335*, 255–266. [\[CrossRef\]](#)
29. Jiang, F.; Zhao, W.; Wu, Y.; Wu, Y.; Liu, G.; Dong, J.; Zhou, K. A polyethyleneimine-grafted graphene oxide hybrid nanomaterial: Synthesis and anti-corrosion applications. *Appl. Surf. Sci.* **2019**, *479*, 963–973. [\[CrossRef\]](#)
30. Lee, W.; Lee, J.U.; Jung, B.M.; Byun, J.-H.; Yi, J.-W.; Lee, S.-B.; Kim, B.-S. Simultaneous enhancement of mechanical, electrical and thermal properties of graphene oxide paper by embedding dopamine. *Carbon* **2013**, *65*, 296–304. [\[CrossRef\]](#)
31. Hummers, W.S.; Offeman, R.E. Preparation of graphitic oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339. [\[CrossRef\]](#)
32. Nazeer, A.A.; Al-Hetlani, E.; Amin, M.O.; Quinones-Ruiz, T.; Lednev, I.K. A poly(butyl methacrylate)/graphene oxide/TiO₂ nanocomposite coating with superior corrosion protection for AZ31 alloy in chloride solution. *Chem. Eng. J.* **2019**, *361*, 485–498. [\[CrossRef\]](#)
33. Wang, N.; Diao, X.; Zhang, J.; Kang, P. Corrosion resistance of waterborne epoxy coatings by incorporation of dopamine treated mesoporous-TiO₂ particles. *Coatings* **2018**, *8*, 209. [\[CrossRef\]](#)
34. ASTM B117-19; Standard Practice for Operating Salt Spray (Fog) Apparatus. ASTM International: West Conshohocken, PA, USA, 2019.
35. Zhang, Y.; Zhang, Z.; Li, J.; Sui, G. (3-aminopropyl) triethoxysilane grafted poly(dopamine)@Fe₃O₄ nanoparticles and their epoxy composites for functional application. *Compos. Part. B-Eng.* **2019**, *169*, 148–156. [\[CrossRef\]](#)
36. Ferrari, A.C.; Meyer, J.C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K.S.; Roth, S.; et al. Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* **2006**, *97*, 187401. [\[CrossRef\]](#)
37. Ozkan, D.; Erarslan, Y.; Kincal, C.; Gurlu, O.; Yagci, M.B. Wear and corrosion resistance enhancement of chromium surfaces through graphene oxide coating. *Surf. Coat. Technol.* **2020**, *391*, 125595. [\[CrossRef\]](#)
38. Shen, L.; Zhao, W.J.; Miao, L.J. Designed a novel EP plus GO/ZRC plus GO coating with bilayered structure for enhancing corrosion resistance of steel substrate. *J. Hazard. Mater.* **2021**, *403*, 123670. [\[CrossRef\]](#)
39. Zhu, X.; Yan, Q.; Cheng, L.; Wu, H.; Zhao, H.; Wang, L. Self-alignment of cationic graphene oxide nanosheets for anticorrosive reinforcement of epoxy coatings. *Chem. Eng. J.* **2020**, *389*, 124435. [\[CrossRef\]](#)
40. Wu, Y.M.; Zhao, W.J.; Qiang, Y.J.; Chen, Z.J.; Wang, L.P.; Gao, X.L.; Fang, Z.W. pi-pi interaction between fluorinated reduced graphene oxide and acridizinium ionic liquid: Synthesis and anti-corrosion application. *Carbon* **2020**, *159*, 292–302. [\[CrossRef\]](#)
41. Zheng, H.; Shao, Y.; Wang, Y.; Meng, G.; Liu, B. Reinforcing the corrosion protection property of epoxy coating by using graphene oxide-poly(urea-formaldehyde) composites. *Corros. Sci.* **2017**, *123*, 267–277. [\[CrossRef\]](#)
42. Bhaskara, S.; Fakrudeen, S.P.; Raju, V.B.; Murthy, H.A.; Raghu, A.V. Comparative studies of inhibitive effects of diamines on corrosion of aluminum alloy in presence of acid media. *Rasayan J. Chem.* **2021**, *72*–78. [\[CrossRef\]](#)
43. Meng, F.D.; Liu, L.; Tian, W.L.; Wu, H.; Li, Y.; Zhang, T.; Wang, F.H. The influence of the chemically bonded interface between fillers and binder on the failure behaviour of an epoxy coating under marine alternating hydrostatic pressure. *Corros. Sci.* **2015**, *101*, 139–154. [\[CrossRef\]](#)
44. Zhu, X.; Zhao, H.; Wang, L.; Xue, Q. Bioinspired ultrathin graphene nanosheets sandwiched between epoxy layers for high performance of anticorrosion coatings. *Chem. Eng. J.* **2021**, *410*, 128301. [\[CrossRef\]](#)
45. Zhou, C.; Hong, M.; Yang, Y.; Hu, N.; Zhou, Z.; Zhang, L.; Zhang, Y. Engineering sulfonated polyaniline molecules on reduced graphene oxide nanosheets for high-performance corrosion protective coatings. *Appl. Surf. Sci.* **2019**, *484*, 663–675. [\[CrossRef\]](#)
46. Necolau, M.-I.; Pandele, A.-M. Recent advances in graphene oxide-based anticorrosive coatings: An overview. *Coatings* **2020**, *10*, 1149. [\[CrossRef\]](#)
47. Yazdani, S.; Prince, L.; Vitry, V. Optimization of electroless Ni-B-nanodiamond coating corrosion resistance and understanding the nanodiamonds role on pitting corrosion behavior using shot noise theory and molecular dynamic simulation. *Diam. Relat. Mater.* **2023**, *134*, 109793. [\[CrossRef\]](#)
48. Xu, W.H.; Han, E.H.; Wang, Z.Y. Effect of tannic acid on corrosion behavior of carbon steel in NaCl solution. *J. Mater. Sci. Technol.* **2019**, *35*, 64–75. [\[CrossRef\]](#)
49. Chang, J.W.; Wang, Z.Y.; Han, E.H.; Liang, X.L.; Wang, G.; Yi, Z.Y.; Li, N.Y. Corrosion resistance of tannic acid, D-limonene and nano-ZrO₂ modified epoxy coatings in acid corrosion environments. *J. Mater. Sci. Technol.* **2021**, *65*, 137–150. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.