



# A long-term anticorrosive coating through graphene passivation

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## ABSTRACT

Despite graphene (G) is impermeable to all molecules and with excellent chemical stability, conductive G is cathodic to most metals and can aggravate metal corrosion at exposed metal-coatings interfaces. This effect may accelerate dangerous localized corrosion and potentially impedes its applications in metal protection. Here, we present successful synthesis of nonconductive G (FmG) through the Diels-Alder reaction between exfoliated G and a bio-based epoxy monomer, and its application in epoxy (EP) anticorrosive coatings. The FmG as-prepared exhibit well solubility in traditional organic solvents due to the graft of FdE chains on the FmG surface. The corrosion resistances of FmG reinforced EP coatings were investigated by electrochemical tests (open circuit potential, Tafel curves, and impedance) after immersed in a 3.5 wt% NaCl solution. The results demonstrated that embedding 0.5 wt% of FmG in EP coating effectively improves the barrier properties of the coating and shows superior corrosion resistance compared with pure EP. In addition, we also gave the protection mechanisms about the corrosion reaction of G-based modified and unmodified EP coatings. The strategy provides a promise strategy for development of G-based heavy coatings with superior barrier properties for metal protection.

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## 1. Introduction

In the recent decades, Graphene (G), a single-atom-thick sheet, has been considered useful in various applications, such as batteries, surface coatings, composites, solar cells and catalysts, owing to its attractive mechanical, electrical, optical and chemical properties [1–4]. As for its application in polymer composite coatings, G is usually used as an effective inorganic filler to improve their barrier properties [5,6]. Yu et al. [7] recently explored the application of G/vinyl polymer composites coatings in corrosion protection. The author found that the G/vinyl polymer composites coatings possess superior corrosion resistance, in which the corrosion protection efficiency increased from 37.90% of blank coating to 99.53% of composite coating with the addition of 2 wt% G. Qiu et al. [8] reported that a polypyrrole (PPy) noncovalent modified G can effectively protect mild steel from corrosion in 3.5 wt% NaCl water solution. Ding et al. [9] reported a similar anticorrosion effect of hydroxyl EP phosphate G for the corrosion protection of Q235

carbon steel. Gu and co-workers [10] reported a detailed study of the anticorrosion property of G-based waterborne EP coatings for electrochemical corrosion of mild steel. They found that the EP coating with 0.5 wt% modified G give a better anticorrosion performance than pure EP coating. It is not surprising that a perfect G-based polymer coating can indeed shield the metal underneath it from corrosion reactions. However, it has also been demonstrated that G-based polymer coating cannot be used as a long-term anticorrosion barrier due to the essential corrosion-promotion activity of G. Even with very low content of G in the polymer matrix, the local corrosion can weaken the coating catastrophically because the galvanic coupling between G and metal substrate [11].

In principle, as a cathodic material, G even if such G/polymer coatings can be fabricated, once damaged during use, are likely to lead to accelerated local galvanic corrosion. To avoid this, and make use of the barrier properties of G for anticorrosion applications, the disadvantages of cathodic coatings should be mitigated. For example, an insulating material (such as a polymer) could be inserted to break the galvanic coupling between G and metal [12–14]. Sun et al. [15] reported that encapsulated G sheets in insulating materials (3-aminopropyl)-triethoxysilane as nanofillers (rGO@APTESs) for polymer coatings. The rGO@APTESs as-obtained is not only molecule impermeability but also insulativity from the insulating materials [16]. On the other hand, if the work function of

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the G can be tuned to become anodic to metal, the galvanic corrosion can be alleviated or even reversed. One possible solution is to add anodic materials, such as zinc, to G/polymer coatings, as indicated in recent trials; Ding et al. [17] prepared G/zinc-containing coatings, in which G played a role in both shielding and electrical conductivity. They found that the channels of electrical contact between the zinc particles as well as zinc and iron was increased due to the conductivity from G, and the utilization of zinc was greatly increased, and as a result the cathodic protection of the polymer coating was enhanced.

In this work, furan epoxide monomer (FdE) was chosen as an insulating encapsulation material to synthesize a nonconductive G (FmG) through Diels-Alder reaction between exfoliated G and FdE. The structure of FmG was characterized by Fourier transform infrared spectrometer (FTIR), Raman spectroscopy, thermogravimetric analyzers (TGA), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), and atomic force microscopy (AFM), respectively. The corrosion resistance properties of FmG reinforced EP composite coatings were investigated by conventional electrochemical measurements in 3.5 wt % NaCl water solution. The tribological behaviors of the coating systems were investigated on UMT-3 tribometer with a ball-on-plate configuration under dry and seawater conditions.

## 2. Experimental section

### 2.1. Materials

Exfoliated G (layers 1–3, purity 99.5%, obtained via solvothermal expansion of graphite followed by sonication assisted exfoliation.) powders were purchased from Coal Chemistry Chinese Academy of Sciences. Furan diepoxide (FdE) was obtained according to our previous work [18]. Double-distilled water (DW) was used throughout the experiments. Epoxy resin (EP) and curing agent (H-4 polyamide) were purchased from Yunda Chemical Co., Ltd. China. All other reagents were purchased from Aladdin and used as received. The Q235 carbon steel electrodes for corrosion tests with the nominal chemical composition (wt.%) of C 0.16, Mn 0.53, Si 0.30, S 0.055, P 0.045 and Fe balance was used as substrate.

### 2.2. Preparation of FdE modified G (FmG)

FmG was carried out in a similar procedure reported by previous

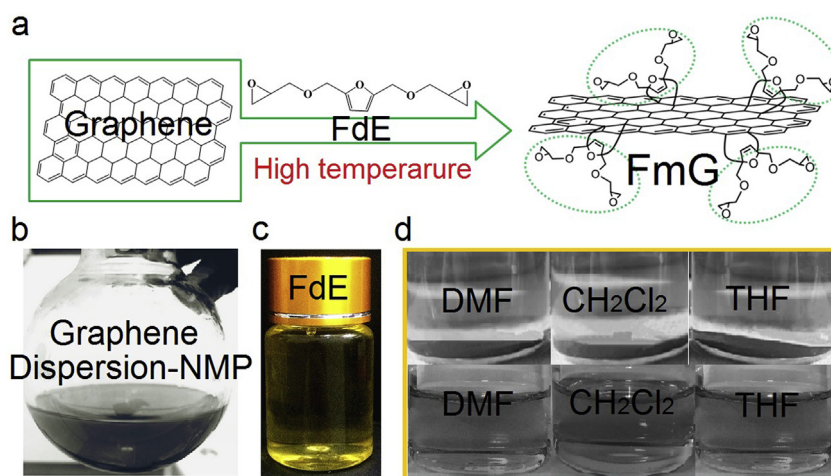
literature [20,21] with some improvements (Fig. 1a): firstly, 100 mg of G was dissolved added into 100 mL of NMP and sonicated for 2 h in a 300 W ice bath sonicator to form a uniform solution. And then, 10 mL of FdE was added. The mixture solution was transferred to a 200 mL Teflon-lined stainless steel autoclave. The sealed autoclave was heated to 100 °C with continuous stirring for 2 h. The FmG was obtained by centrifugation (TG610, 10, 000 rpm) and repeatedly rinsed with acetone to remove the unreacted FdE until the filtrate became colorless.

### 2.3. Preparation of coating systems

Before coating, Q235 carbon steels ( $2 \times 2 \text{ cm}^2$ ) were polished with 500–1500 grit sandpapers, then rinsed with distilled water for several times, and being degreased by ultrasonication in acetone, finally blow-dried and kept in a desiccator prior to painting. The FmG/EP composite coatings with 0.2 wt%, 0.5 wt%, 1.0 wt%, and 0.5 wt% of G were fabricated as follows: 20 mg of FmG was uniformly dispersed in 20 mL of  $\text{CH}_2\text{Cl}_2$  with ultrasonic treatment for 1 h. Subsequently, E44 epoxy resin was added in the solution and was magnetically stirred for 30 min. Finally, the curing agents were added into the system and the mixtures were mixed thoroughly with high speed blender at 4000 rpm for 5 min, and air bubbles were removed under vacuum at room temperature for 10 min. The mixtures were coated on the surfaces of pre-treated Q235 carbon steel substrates using a wire bar coater with thickness of 20  $\mu\text{m}$ . The cured reactions of composite coatings were conducted at 40 °C for 12 h and the thickness was  $20 \pm 2 \mu\text{m}$ . Similarly, 0.5, and 1.0 of FmG coatings were prepared and the obtained specimens are denoted as FmG<sub>0.2</sub>, FmG<sub>0.5</sub>, and FmG<sub>1.0</sub>, respectively. For example, FmG<sub>0.2</sub> represents the EP composite containing 0.2 wt. % FmG. For comparison purpose, the pure EP and G-based (0.5 wt% of unmodified G) EP composite coatings with 0.5 wt% of initial G were also prepared, and specimens are denoted as FmG<sub>0</sub> and G<sub>0.5</sub>.

### 2.4. Measurements and characterization

The resistance values of graphene films are carried out by using a digital multi meter (AT9205A, 200  $\Omega$ –200 M $\Omega$ ) at room temperature, and the corresponding electrical conductivity was calculated based on the electrical resistivity. Fourier transform infrared spectrometer (FTIR, THERMO Nicolet 6700) was used to confirm



**Fig. 1.** Schematic illustration of FmG (a), the G NMP dispersion (b), FdE (c), and the different G (the upper row) and FmG (the lower row) dispersions in a concentration of 0.1 mg/mL. (A colour version of this figure can be viewed online.)

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