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Synthesis of graphene oxide nanosheets functionalized by green corrosion inhibitive compounds to fabricate a protective system

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ABSTRACT

The adsorptive behavior of Urtica Dioica (U.D) leaf extract on the graphene oxide nanosheets (GONs) was examined by experimental and density functional theory (DFT) approaches. Experimental results demonstrated the strengthened adsorption of the Urtica Dioica leaf extract on the GO sheets at acidic pH of 2, leading to the corrosion inhibition of mild steel in chloride solution. It was observed that the inhibition effects of GO-U.D sheets enhanced in the presence of Zn^{2+} cations in solution and coating phases. The DFT results revealed the physisorption and chemisorption of inhibitors onto GO surfaces.

1. Introduction

Application of epoxy coating (EP) on the metallic substrates is the most conventional and popular method for corrosion protection against corrosive environments through creation of a physical barrier between the corrosive agents and steel surface [1–4]. Due to the high cross-linking density and other structural properties, this kind of coating shows good corrosion protection properties, high chemical stability, low shrinkage, excellent adhesion and high thermal stability [5,6]. However, the EP has some disadvantages, such as high brittleness, poor flexibility and impact resistance, resulting in the creation of plentiful tiny pores and cracks in the coating matrix during coating fabrication, application and/or curing process [7,8]. The microscopic defects present in the coating matrix are conductive pathways that the corrosive agents can easily diffuse into the coating structure and finally reach the coating/metal interface, leading to the coating delamination as a result of cathodic reaction and corrosion products creation due to anodic dissolution of steel. Moreover, the corrosive electrolyte attacks the coating structure, leading to the coating deterioration. So obtaining long term corrosion protection properties without elimination of these weaknesses seems impossible [9,10]. One strategy to overcome these problems and reach a coating system with enhanced corrosion protection performance is reinforcing the coating with fillers and/or pigments. There are a plenty of fillers and pigments in this regard but the use of nanoparticles has been attracted a great deal of the researchers' attention in recent years [11–16].

Recently, graphene and graphene oxide nanosheets have been introduced as an advance type of carbon nanomaterials with superior properties i.e., electrical, mechanical, chemical, thermal and barrier properties [2,17–28]. Among different types of carbon nanomaterials, the graphene oxide (GO) has attracted great attention of the researchers. The potential of graphene oxide as an effective barrier nanosheet comes from its impermeability to oxygen and water and very high surface area and nanometric thickness. However, the GO dispersion in polymers is still a big challenge. The GO nanosheets tend to interact with each other through weak van der Waals forces, leading to aggregation and decline in polymer matrix protection performance. Covalent and non-covalent functionalization of the GO nanosheets is considered in this regard [21–25].

The effect of GO nanosheets on the corrosion protection performance of the polymer coatings has been studied in last three years. In our previous works, we have demonstrated that addition of covalently functionalized GO with polyisocyanate [29], diamine [30], amino silane [31,32], and SiO_2 nanoparticles [33] could effectively enhance the GO nanosheets compatibly and dispersion properties in the epoxy, polyurethane and silane sol-gel based coating, providing coating system with superior barrier performance against water and corrosive agents. Yu et al. [34] investigated the effect of GO sheets modified with titanium dioxide on the corrosion protection performance of epoxy coatings. Mo et al. [35] reported effective corrosion protection performance of polyurethane composite coatings reinforced with functionalized graphene and graphene oxide nanosheets. The corrosion protection improvement of epoxy coating after addition of graphene oxide–-zirconia dioxide has been reported by Di et al. [36]. Yu et al. [37] revealed that inclusion of graphene oxide–alumina hybrids into the epoxy coating provides effective corrosion protection performance. Liu et al.

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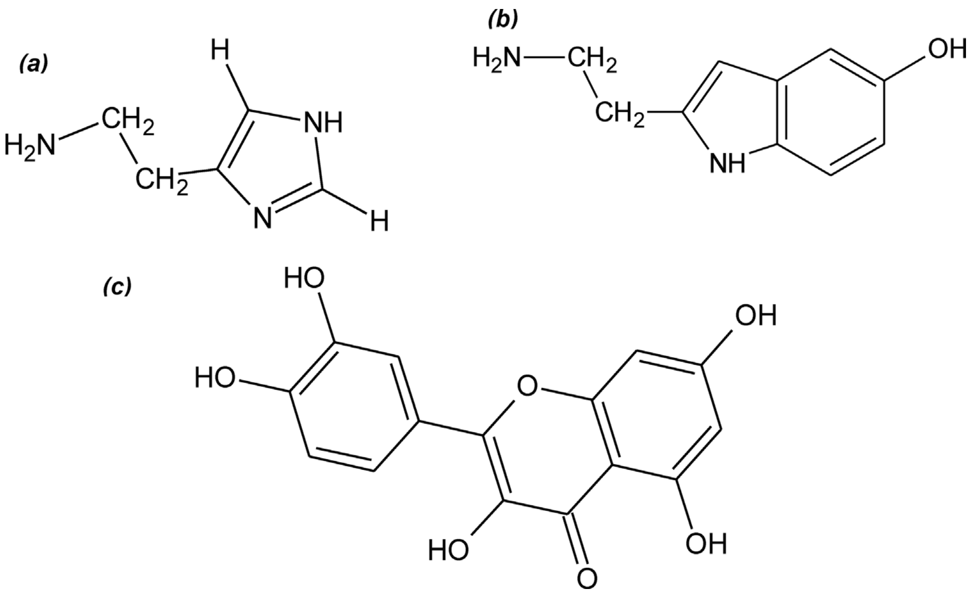

Fig 1. Structural formula of some examples of organic compounds existed in U.D extract; (a) hystamine, (b) serotonin, and (c) quercetin.

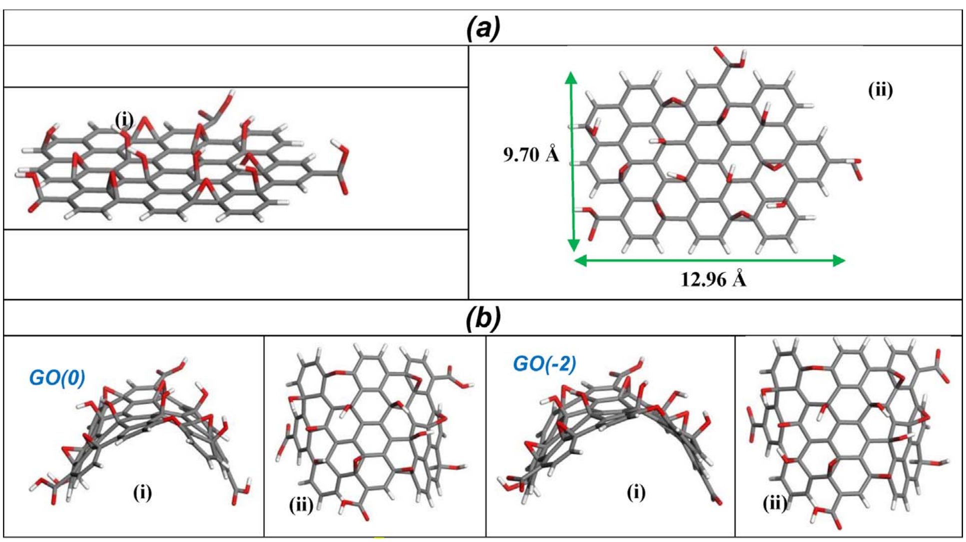

Fig. 2. (a) The side and top views of the initial geometry of considered GO model, and (b) its corresponding B3LYP/6-31G(d,p) optimized structures. The GO(0) is neutral molecule and GO(-2) denotes the GO with two deprotonated carboxyl groups (i.e., surface charge of −2 e).

[38] revealed the enhanced corrosion resistance properties of epoxy composite coatings reinforced with functionalized fullerene C60 and graphene. Li et al. [39] showed corrosion protection performance improvement of silane composite after addition of silanized graphene oxide. In a research done by Liu and his coworkers [40] they showed that inclusion of graphene nanosheets into the waterborne epoxy coating resulted in remarkable improvement in its corrosion resistance. All of the aforementioned researches suggest a similar fact that addition of GO nanosheets to the polymeric coatings can only improve their protection ability through enhancing the barrier properties. This means that in the case of slight or harsh mechanical damages creation in the coating matrix the GO sheets cannot provide any protective performance, which is the main shortcoming of the GO-polymer composites. To the best of authors' knowledge, there is no study addressed the fabrication of GO nanosheets with both barrier and active inhibition performance.

In this work, it was intended to add inhibition properties to the GO nanosheets through adsorption of inhibitive agents onto the surface of GO sheets. Different types of corrosion inhibitors were candidates for doing this experiment but it was decided to work on environmentally friendly inhibitors extracted from the plants leaves, which are cheap, readily available in large amount and biodegradable. Among various green corrosion inhibitors the Urtica dioica, often called nettle leaf, is considered. The fresh nettle leaf contains different organic compounds, e.g. hystamine, serotonin, flavonal glycosides such as quercetin, as well as carotenoids, acids, chlorophyll, vitamins (e.g. C, B and K), and minerals (e.g. calcium, magnesium, and potassium) [41]. The corrosion inhibition properties of nettle leaf extract have been previously studied [42,43]. However, there are no report on the use of nettle leaf extract on the GO nanosheets and its effect on the corrosion protection properties of an epoxy coating.

The inhibition effect of GO-U.D was studied in solution and coating phases. The GO-U.D extracts in 3.5 wt.% NaCl solution were prepared and then the corrosion resistance of the steel samples was studied through EIS and polarization tests. The GO-U.D at optimum adsorption pH was added to the epoxy coating and their influences on the coating corrosion protection behavior were examined by EIS and salt spray tests after creation of an artificial defect. Furthermore, ab initio quantum mechanics (QM) calculations applying density functional theory (DFT) were directed towards the GO-nettle leaf extract complexes to get a detailed electronic/atomic-level understanding concerning the interaction and interfacial bonding between nettle leaf extract and GO surfaces at different pH conditions.