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# Layer-by-Layer Self-assembled Graphene Oxide Nanocontainers for Active Anticorrosion Application

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This work presents the synthesis of a new type of graphene oxide nanocontainer and their application for developing active anticorrosion coatings. The graphene oxide nanocontainers encapsulated with polymeric ionic liquid, a corrosion inhibitor, were prepared through a facile procedure based on layerby-layer assemble technology. The variations of zeta potential confirmed the construction process of nanocontaiers. Electrochemical impedance spectroscopy was employed to investigate the anticorrosion performance of composite coatings. Results indicated that the introduction of nanocontainers significantly enhanced the corrosion resistance of polymer coatings. The embedded polymeric ionic liquid could exert its corrosion inhibition effect at defects interface, providing active anticorrosion ability for coating. Meanwhile, the durable passive anticorrosion property was also possessed, which attributed to the impermeable graphene oxide nanosheets. This novel nanocontainer endowed the coating system with superior barrier property and corrosive inhibitor function.

Keywords: nanocontainer, graphene, coating, active anticorrosion

# **1. INTRODUCTION**

The widely used metallic materials in industrial, including steel, aluminum, and their alloys, are susceptible to metal corrosion, which causes metal degradation and economic losses [1, 2]. Application of organic coatings is considered as one of the most commonly used strategy for metallic protection through isolating metal substrate from corrosive mediums [3-5]. However, two deficiencies of organic coating are existed: (1) the applied organic coatings are composed of polymer molecular chains, they are

not completely impermeable to electrolytes; (2) the organic coating can only provide a passive barrier effect for metals, while their protective function will become invalid once the coating defects produced [6-8]. In this sense, the design of coating system with not only passive barrier but also active inhibition properties could be a promising means to handle the above challenges.

To obtain an active anticorrosion functionality, polymerizable agents or/and corrosion inhibitors were embedded in microcapsules or nanocontainers and then uniformly dispersed in coating matrix [9, 10]. For microcapsules-based coatings, the curing components such as dicyclopentadiene [11, 12], linseed oil [13-16], siloxane [17] and epoxy [18, 19] were encapsulated in microcapsules. When the micro-cracks formed and started expanding in coating matrix, the curing agents were released for subsequent healing the defect by polymerization process [20]. Generally, large size of capsules is necessary to guarantee a better repair result. However, the oversized capsules are detrimental to coatings integrity [21], which closely relates to the integral protection performance. In another way, embedding corrosion inhibitors using nanocontainers to develop active/self-healing anticorrosion coatings was also performed [22-25]. Due to the corrosion protection of inhibitor is based on their adsorption behavior on metal surface, a small amount of inhibitors is sufficient to form a protective layer and thereby decreasing the metal corrosion reactivity [26, 27]. Among the above mentioned capsules-based coating systems, the studied microcapsules or nanocontainers could only provide active protection for metal substrate, while its barrier effect is limited due to their geometric shape (spherical or mesopores materials).

Graphene and graphene oxide (GO), as a class of two-dimensional materials, have been widely employed as an effective barrier to fabricate anticorrosion coatings due to their superior mechanical property, high aspect ratio and excellent impermeability [28-30]. The barrier property of composite coatings to corrosive mediums was improved greatly after incorporation of graphene [31, 32] or functionalized GO nanosheets [33-35]. To provide a durable anticorrosion protection for metallic substrate, the combination of passive barrier property and active inhibition functionality is necessary. Therefore, we synthesized a new type of GO-based nanocontainers in this study by using layer-by-layer self-assemble technology. Polymeric ionic liquid (PIL), an environmentally friendly corrosion inhibitor [36-38], has been embedded within polyelectrolyte deposited layers. The resulting containers-based coatings present an enhanced long-term protection and efficient active inhibition function, which attributed to the impermeable of GO and corrosion inhibitive of PIL.

# 2. EXPERIMENTAL SECTION

#### 2.1 Materials

Graphite, N-vinyl-imidazole, 1-bromobutane, ethyl acetate, 2,2'-azobis(2-methylpropionitrile) (AIBN) and poly (4-styrenesulfonic acid) (PSS) were purchased from Aladdin Industrial Corporation. Waterborne epoxy resin (E51) and curing agent were obtained from Hangzhou Hanma Paint & Coatings Co., Ltd. The metal electrode was prepared using carbon steel substrate with a working area of 1 cm<sup>2</sup>, which was polished by 400 and 800 C sand papers and cleaned with acetone and ethanol, respectively.

#### 2.2 Synthesis of PIL

An imidazole-based PIL was synthesized and encapsulated in GO nanocontainers. Firstly, the Nvinyl-3-butylimidazolium bromide IL monomer was prepared [39], as revealed in Fig. 1a. In a typical procedure, N-vinyl-imidazole (4.70 g, 0.05 mol), 1-bromobutane (8.22 g, 0.06 mol) were dissolved in 20 mL anhydrous ethanol to obtain a homogeneous solution and then placed in a preheated oil bath (80°C) with continuous stirring. After 24 h of reaction, the resultants were purified through adding into a mixture of ethyl acetate and ethanol three times. Finally, the IL was obtained after removing the solvents via rotary evaporator.

The PIL was synthesized through a conventional radical polymerization method [40, 41], and the schematic illustration for the synthesis process was also presented in Fig. 1b. A round-bottom flask was charged with 2 g of prepared IL monomer and 20 mL of anhydrous ethanol. Then, 5 mL of ethanol solution containing 10 mg of AIBN was dropped into the flask. To obtain a protective atmosphere, the mixture was purged with nitrogen gas for 1 h. The polymerization reaction was carried out under 60 °C with mechanically stirring for 24 h. After removing the solvents in vacuo, the PIL was achieved.

#### 2.3 Preparation of graphene oxide-based nanocontainers

In this study, the modified Hummer's method was used to oxidize nature graphite to GO nanosheets [40]. Typically, 0.5 g of nature graphite powder was added into 30 mL of H<sub>2</sub>SO<sub>4</sub> solution (98 %) under ice bath with constant stirring. After 2 h reaction, 2.5 g of KMnO<sub>4</sub> was added slowly and the temperature was kept less than 20 °C. The oxidation reaction was progressed for another 24 h under ambient temperature. After that, 500 mL of deionized water was added to dilute the resultant suspension, which was further treated with H<sub>2</sub>O<sub>2</sub> to complete the oxidation process. Subsequently, the mixture was centrifugation and washing with hydrochloric acid and deionized water thoroughly and vacuum drying at 50 °C to obtain the GO powder.

Layer-by-layer self-assemble technique was employed to construct the GO-based nanocontainers as shown in Figure 1c. The initial GO nanosheets are negatively charged (pH = 8), and the deposition of the positive PIL was carried out by mixing 50 mL of 2 mg/mL GO suspension and 10 mL of 3 mg/mL PIL solution for 1 h. The GO/PIL sample was washed with deionized water three times and separated via centrifugation. It should be noted that the washing treatment was implemented for the sample after each deposition procedure. Then, the deposition of negative layer was realized by mixing 10 mL of 3 mg/mL PSS solution with separated GO/PIL. To enhance the inhibitor loading capacity, the above two procedures (PIL and PSS) were performed twice, respectively. After the completion of deposition, the GO-based nanocontainers was obtained with a structure of GO/PIL/PSS/PIL/PSS.



**Figure 1.** Fabrication process of (a) N-vinyl-3-butylimidazolium bromide IL and (b) PIL; (c) schematic illustration of the synthesis route of graphene oxide based nanocontainers.

# 2.4 Fabrication of composite coatings

For the preparation of containers impregnated composite coatings, the homogenous dispersion of containers was firstly prepared by dissolving 50 mg of nanocontainers in 5 mL water. Then, 3 g of waterborne hardener was mixed with above suspension. After magnetic stirring for 20 min, this mixture was processed with ultrasonication for another 1 h. The remaining solvent was removed through rotary evaporator, and the epoxy resin (2 g) was added. To ensure the compactness of coatings, the degassing process was performed in vacuum oven to eliminate the bubbles. Subsequently, the coated electrode with thickness of  $50 \pm 3 \mu m$  was obtained using a bar coater after curing for 72 h, which was defined as FGO/EP coating. In addition, the pure epoxy coating (EP) and the coating with GO (GO/EP) were also prepared in a similar way.

## 2.5 Characterization

The structure properties of prepared nanocontainers were characterized by FTIR (Nicolet 6700, USA), Raman (Renishaw in Via Reflex) spectroscopy and Zeta potential (Delsa Nano C Submicron, Beckman Coulter Delsa, Krefeld, Germany) measurements. FTIR spectra were collected from an FTIR spectrometer with a resolution of 1 cm<sup>-1</sup> between 400 and 4000 cm<sup>-1</sup>. Besides, scanning electron microscope (SEM, HITACHI S4800) and transmission electron microscope (TEM, JEOL2100) were used to estimate the morphology of nanocontainers.

The protective performance and failure process of composite coatings were evaluated using electrochemical impedance spectroscopy (EIS), which was conducted on an electrochemical working station (CHI660E) in 3.5 wt% NaCl solution. The EIS test was performed at the frequency range of 100 kHz to 10 mHz with a sinusoidal perturbation of 20 mV amplitude. Besides, the EIS test was equipped with a conventional three-electrode cell system, including the counter electrode (platinum plate with 2.5 cm<sup>2</sup> area), reference electrode saturated calomel electrode (SCE), and working electrode (coated mild steel with an exposed area of 1 cm<sup>2</sup>). To ensure the reproducibility, three samples were needed for each kind of coatings. After the EIS test, the surface morphology of coated electrodes was observed through SEM.

#### **3. RESULTS AND DISCUSSION**

#### 3.1 Characterization of nanocontainers

The FTIR spectra were collected after each of the deposition steps to reveal the detailed process of preparing of the GO nanocontainers. As can be seen from Figure 2, the characteristic peaks of GO were presented at 3420, 1722 and 1059 cm<sup>-1</sup>, which correspond to hydroxyl (-OH), carbonyl stretching (-C=O) and alkoxy vibrations, respectively [43, 45]. Additionally, the C=C stretching was observed at 1628 cm<sup>-1</sup>. Compared with GO, some new peaks were displayed accompanied with the deposition layers. The presence of in-plane asymmetric stretching (1167 cm<sup>-1</sup>) arising from imidazolium ring for Figure 2b, which confirms the formation of PIL on the GO surfaces. After deposition of PSS, the aromatic ring vibrations (1473 cm<sup>-1</sup>) were observed, providing an evidence of attachment of polyelectrolytes [45, 46]. Moreover, the -CH (2927 cm<sup>-1</sup>) and -CH<sub>2</sub> (2859 cm<sup>-1</sup>) bands were also exhibited [46, 47], further suggest that the PIL is successful assembled into nanocontainers.



Figure 2. FTIR spectra of: (a) GO; (b) GO/PIL; (c) GO/PIL/PSS; (d) GO/PIL/PSS/PIL; (e) GO/PIL/PSS.

Raman spectroscopy was employed to analyze the nanocontainers during the deposition process. From Figure 3, two prominent bands appeared at 1348 (D band) and 1575 (G band) cm<sup>-1</sup>, which indicate the vibration of sp<sup>3</sup> carbon atoms from the functional groups and the in-plane vibration of sp<sup>2</sup> carbon atoms [48], respectively. Usually, the deviation degree of graphene crystal structure could be reflected from the variation of the intensity ratio of D and G bands ( $I_D/I_G$ ). Therefore, the deposition process of PIL and PSS can be estimated through comparing the change of this ratio. The intensity value ( $I_D/I_G$ ) of pristine GO was about 0.87, relating to the functional groups at the graphene surfaces. With the deposition of electrolyte layers, this value was increased to approximately 0.98, signifying the variation of graphene structure. This can be attributed to the interaction between GO and assembled layers. In addition, the G band was red-shifted during the construction of nanocontainers, confirming the existence of charge transfer between GO and polyelectrolytes [49].



Figure 3. Raman spectra of: (a) GO; (b) GO/PIL; (c) GO/PIL/PSS; (d) GO/PIL/PSS/PIL; (e) GO/PIL/PSS/PIL/PSS.



**Figure 4.** Variations of Zeta potential during the preparation of nanocontainers; Layer number 1: GO; 2: GO/PIL; 3: GO/PIL/PSS; 4: GO/PIL/PSS/PIL; 5: GO/PIL/PSS.

The surface charging variation of nanocontainers deposited with adsorbed polyelectrolytes or inhibitor layer was estimated by using Zeta potential measurement (Figure 4). Usually, the GO nanosheets exhibit negative charge (-23.8 mV) in weak alkaline solution due to the ionization of carboxyl groups [50]. An increase of surface charge (5.5 mV) was exhibited after the deposition of PIL layers. As the PSS layers deposited, the surface charge decreases to -20.1 mV. The deposition procedures of PIL and PSS were carried out twice with opposite electrical charges, ensuring more corrosion inhibitors were encapsulated in nanocontainers. The surface charge changes accompanied with deposition process, which apparently revealed the construction process of nanocontainers through layer-by-layer assemble technique.

## 3.2 Morphology of the graphene oxide-based nanocontainers

SEM and TEM measurements were employed to examine the morphology and microstructure of GO and prepared nanocontainers. It can be observed that the GO nanosheets present a thin laminar structure with smooth surface (Figure 5a). Besides, the transparent texture for GO was also observed through TEM test (Figure 5c). As for the prepared nanocontainers, a rough surface with unevenly distributed wrinkles were displayed, which attributed to the introduction of assembled layers (Figure 5b). After the deposition process, the obtained nanocontainers still maintain an intact slice structure as observed in Figure 5d. These observations confirmed that the PIL and PSS layers were successfully deposited on GO surfaces, and the nanocontainers were also prepared.



Figure 5. SEM images of (a) GO and (b) nanocontainers; TEM images of (c) GO and (d) nanocontainers.

#### 3.3 Fracture surfaces of containers-based coatings

The anticorrosion performance of composite coatings is largely dependent on the impermeability or compactness of coating matrix, which relates to its barrier performance. Generally, a coating matrix with better compactness will exhibit high resistance for corrosive ions penetration. Therefore, the morphologies of fracture surface for the composite coatings were observed via SEM. Prior to observation, the coating samples were immersed in liquid nitrogen and then broken swiftly to create a fracture surface. As for pure epoxy (Figure 6a), unevenly distributed holes derived from solvents volatilization were observed in fracture surface, signifying its poor impermeability. After incorporation of GO nanosheets or nanocontainers, the fracture surface of composite coatings displayed numerous wrinkles due to the interface interactions between resin and graphene. Besides, the nanocontainers-based coating exhibits improved denseness with less holes and coating defect depicted in Figure 6c. Thus, it can be concluded that the prepared nanocontainers can be well dispersed in coating matrix and the compatibility between GO and coating matrix does not been affected by the assembled layers.



Figure 6. SEM images of the fracture surfaces for (a) pure EP, (b) GO/EP and (c) FGO/EP coatings.

## 3.4 Active anticorrosion properties of nanocontainers-based coatings

To study the active protection ability of composite coatings, the EIS test was carried out on the scratched samples in 3.5 wt% NaCl solution. The electrochemical impedance for scratched samples with

different immersion time were presented in Figure 10. It can be observed that the scratched samples for pure EP and GO/EP coatings displayed obvious impedance drop with the immersion period (Figure 7a and 7b), signifying the metal oxidation reaction. These results revealed that the protective property cannot be maintained for the EP and GO/EP coatings when coating defects generated. In terms of FGO/EP coatings, the impedance modules are higher than those of EP and GO/EP coatings during the whole period. After a decrease from  $4.12 \times 10^5$  to  $3.01 \times 10^5 \Omega$  cm<sup>2</sup>, these values are gradually increased to  $5.54 \times 10^5 \Omega$  cm<sup>2</sup> (Figure 7c), which is higher than other coatings. In previous report, Qian et al. [23] prepared a new type of nanocontainers using SiO<sub>2</sub> nanoparticles coated with chitosan/alginate layers. The resultant coatings exhibit self-healing functionality after the coating has defects. However, the impedance values for scribed coating in our study are higher than the reported results. In the defect interface, the encapsulated PIL could adsorbed on exposed steel surfaces to exhibit their corrosion inhibitive function. Therefore, the charge transfer process could be impeded to some degree, and the exposed substrate could be isolate from the electrolytes. These can be interpreted that the prepared nanocontainers could endow the polymer coating with active anticorrosion performance.

The impedance values were collected at an open circuit potential (OCP). Therefore, the change of OCP as a function of time can be considered as a reference to measure the tendency of metal corrosion reaction. Figure 7d shown the variation of OCP of scratched samples for 120 h immersion. Generally, the more negative the OCP value for the electrode system, the more easily the metal is corroded.



**Figure 7.** Bode-phase plots of scratched coatings after different immersion time in 3.5 wt% NaCl solution.

As can be seen from Figure 7d, the OCP values for pure EP and GO/EP coating are within the extent of  $-0.70 \sim -0.64$  mV, suggesting the serious metallic deterioration deriving from the fast penetration of electrolyte. However, more positive OCP values were observed for containers-based coatings. The positive shift of OCP values indicat an improved corrosion protection of metal substrates.

These results indicated that the FGO coating could continue to play a protective function through the embedded corrosion inhibitor even if the coating is defective.

# 3.5 Passive protection performance of composite coatings

Organic coatings are generally considered to be an insulating layer, which can protect the metal substrate from corrosion by preventing or delaying the penetration of electrolytes. As we know, the barrier property and the active anticorrosion functionality are two essential factors for designing an effective anticorrosion coating. To further explore the functionality of nanocontainers on the passive anticorrosion performance of composite coatings, the EIS measurement was performed in a long period (40 days). Different reactivity of metal corrosion reaction will display with electrolytes penetrate into coating matrix. The corresponding electrochemical elements can be reflected from the EIS results. Usually, a coating system with less water penetration will exhibit a higher impedance modules at the lower frequency ( $Z_{f=0.01\text{Hz}}$ ), which could be considered as a parameter to evaluate the coating's barrier property [51, 52]. As can be seen from Figure 8a, a higher electrochemical impedance modules ( $Z_{f=0.01Hz}$ ) was observed for all samples after one day immersion, indicating that the moisture does not reach the coating/metal interface. The difference of impedance values becomes significant for the samples with the immersion time. For the pure EP, these values decreased from  $3.89 \times 10^8 \Omega$  cm<sup>2</sup> (1d) to  $4.47 \times 10^6 \Omega$  $cm^2$  (40d), which resulted from the penetration of electrolytes and revealed the coatings failure. Compared with EP coating, the impedance values were increased after incorporation of GO due to the enhanced water resistance. Obviously, the impedance values for FGO/EP coating were maintained above  $10^8 \ \Omega \ cm^2$  even after 40 days test, which are higher than EP and GO/EP coatings. This result was consistent with a previous report by Cheng et al. [26] In their study, an intelligent anticorrosion coating was designed based on encapsulation of BTA in synthetic SiO<sub>2</sub> nanocontainers. After 30 days immersion, the impedance values  $(Z_{f=0.01Hz})$  for nanocontainers based coatings are decreased to about  $10^7 \,\Omega \,\mathrm{cm}^2$ . However, the nanocontainers developed in our study significantly enhanced the impedance values of composite coatings to above  $10^8 \Omega$  cm<sup>2</sup> even after 40 days. The introduction of nanocontainers enhanced the impermeability of coating system, and prevented the direct penetration of corrosive ions.

In addition, the Bode-phase plots were also employed to analysis the process of coating degradation. These spectra can be generally divided into high and low frequency regions, which correspond to the coating capacity and pore resistance in t0he coating surface and the double-layer capacity and the resistance of the metal corrosion reaction, respectively [53]. The number of time constants can be reflected from the Bode-phase plots, which denote the metal oxidation degree. Two time constants were observed for pure EP coating after 10 days immersion (Figure 8b). In this situation, the electrolytes have penetrated into metal/coating interface and the metal oxidation reaction has also happened. The control step of corrosion reaction has been transformed from coating resistance to charge transfer resistance. After 20 days immersion, the Warburg resistance was presented, which denotes the diffusion behavior. The presence of Warburg resistance revealed that the coatings barrier property is invalid and the permeation channel in coating matrix is formed. The fast failure results illustrated the poor corrosion resistance of waterborne EP coatings. For the GO/EP coatings, the water penetration

process has been suppressed to some extent (Figure 8c). Obviously, even after 40 days immersion, the second time constant was not apparent for FGO/EP coating as presented only one arc in Bode-phased plots. The GO nanosheets improved the impermeability of composite coatings. Simultaneously, the encapsulated corrosion inhibitor (PIL) could exhibit its inhibition effect by adsorbing on metal surfaces when the coating defects appeared. Therefore, this novel nanocontainers effectively enhanced the long term protective performance of composite coatings.

Furthermore, the EIS spectra were fitted through ZSimpWin software using the equivalent circuit shown in Figure 9 to better understand the degradation processes and the contributions of nanocontainers to the studied coating systems. In the circuits, the coating resistance ( $R_c$ ) and coating capacitance ( $Q_c$ ) reflect the coating response under electrolyte, while the charge transfer resistance ( $R_{ct}$ ) and double-layer capacitance ( $Q_{dt}$ ) describe the metal oxidation process, respectively. The  $R_c$  value can be considered as an indicator to reflect the degree of coating defects (pores and cracks) [54]. A coating system with better barrier properties usually exhibit a high  $R_c$  value [55]. It can be observed from Figure 9d, the containersbased coatings (FGO) showed the highest  $R_c$  value among all samples during the hole tested period. This might due to fewer defects formed in the coating or less area of coating delamination after incorporation of nanocontainers. Besides, the  $R_{ct}$  value can be used to describe the corrosion degree of metal substrate, which relates to the electrochemical reaction at the interface of metal substrate. All samples exhibited decreased trend, while the  $R_{ct}$  values for FGO/EP coating are higher than pure EP and GO/EP coating even after 40 days immersion (Figure 9e). The impermeable GO nanosheets impeded the direct penetration of electrolytes and the PIL embedded in nanocontainers protected the metal substrate from corrosion.



**Figure 8.** Bode plots of different coating systems immersion in 3.5 wt % NaCl solution: (a) 1 day, (b) 10 days, (c) 20 days and (d) 40 days.



**Figure 9.** Electrical equivalent circuit models for composite coatings: (a) $\sim$ (c); variation of the electrical parameters of  $R_c$  (d) and  $R_{ct}$  (e) collected from fitting results.

# 3.6 Morphology of rust layers on steel substrate after EIS test

For visualization of the barrier performance and active anticorrosion of the containers-based coatings, the morphology of steel electrodes was observed after removing coatings. The electrode coated with pure EP coating provided only limited passive protection, displaying unsatisfactory anticorrosion ability and the steel surface was covered with loose corrosion products (Figure 10a). This might be resulted from the rapid penetration of corrosive mediums and demonstrated the severe metal degradation. Once there is corrosive products between metal and coating matrix, the coating adhesion will be reduced, which will result in peeling of the coating. From Figure 10b, the metal oxidation degree had been mitigated for the samples with direct introduced GO. Apparently, the steel electrode coated with FGO/EP coating exhibited a relative smooth surface with small amount of corrosion products as observed from Figure 10c. This was attributed to the superior impermeability of GO nanosheets and corrosion inhibition function of PIL. In other words, the prepared nanocontainers could largely inhibit the penetration of corrosive medium and effectively improve the anticorrosion performance of epoxy coatings.



Figure 10. SEM images for steel substrate beneath (a) pure EP, (b) GO/EP and (c) FGO/EP coatings after EIS test.

# 4. CONCLUSIONS

In this work, we have synthesized a new type of graphene oxide-based nanocontainers by using layer-by-layer assembly of GO, PIL and PSS. The potential application of nanocontainers for anticorrosion was also evaluated. The prepared nanocontainers displayed a lamellar structure as observed through SEM and TEM. The protective performance of epoxy coatings doped with nanocontainers was investigated by EIS measurement. Results indicated that the long term anticorrosion performance of coatings was improved significantly after incorporation of nanocontainers. More importantly, an active anticorrosion function was displayed, which attributed to the corrosion inhibition effect of embedded PIL. Therefore, this novel nanocontainers developed in this study exhibited both impermeable property and inhibitor encapsulating capability, which present great potential for practical applications.

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