

# In-situ bonding technology and excellent anticorrosion activity of graphene oxide / hydroxyapatite nanocomposite pigment

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## ABSTRACT

The design synthesis of new anticorrosive pigments for reducing disasters and energy consumption is of great significance. Here, graphene oxide-hydroxyapatite (GO-HAP) nanocomposite with stable structure is fabricated via in-situ bonding technology. The interlaced structure of GO-HAP nanocomposite protects the steel substrate from attack by the corrosive species. Moreover, the free aggressive  $\text{Cl}^-$  ions can be immobilized by the replacement with the hydroxyl groups in HAP crystal to generate stable chlorapatite, further defending the steel substrate from destruction. In addition, the electrons released from the anode can be collected by GO sheets for inhibiting the cathodic reaction. Thus, the GO-HAP nanocomposite, as an anticorrosion pigment, exhibits a remarkable anticorrosion performance. In comparison with blank epoxy resin system, the impedance value of 0.6% GO-HAP/epoxy increases by 754.4%. The synergistic complementation mechanism of GO and HAP enriches metallic anticorrosion theory and provides a new thought for synthesis of novel and promising anticorrosive pigments.

## 1. Introduction

The serious economic loss caused by metal corrosion has stimulated the researchers to explore more efficient anticorrosion pigments [1]. Although inorganic anticorrosive pigments have undergone a reform from the highly effective chromate to the environment-friendly zinc phosphate, effective and green anticorrosive pigments are still few [2–4]. The types and properties of anticorrosive pigments still need to be enriched and improved. During the process of corrosion, the aggressive  $\text{Cl}^-$  ions permeating into the epoxy coating play a crucial role in the charge transfer between electrolytes and steel substrates [5]. In general,  $\text{Cl}^-$  ions are insulated from the metallic substrate by physical shielding effect. However, it is also important for metal protection to eliminate aggressive  $\text{Cl}^-$  ions invading into the system. In consequence, searching for anticorrosion pigments that can convert  $\text{Cl}^-$  ions into stable substances to defense other corrosive species is necessary.

Hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , HAP) is a kind of eco-friendly and nontoxic functional material [6–9]. It presents the stable chemical properties [10], good adhesion to metal [11], significant adsorption ability and low water solubility [12]. At present, few researches about the application of the low-cost HAP in metal protection have been reported. D. Snihirova et al. considered HAP as a reservoirs of corrosion

inhibitors which released the active inhibiting species on demand [13]. But the anticorrosion activity of HAP has not been discussed in detail. Good adsorption property facilitates the cationic and anionic exchange between HAP and other substances [14]. Derived from this, a novel anticorrosion mechanism of HAP can be conjectured:  $\text{Cl}^-$  ions can be converted to form stable chlorapatite through substitution with  $\text{OH}^-$  in HAP. Nevertheless, the chemical stability of HAP ( $K_{sp} = 1.58 \times 10^{-58}$ ) [15] makes it hard to exert anticorrosion performance in early immersion. As a result, the modification is essential to compensate this flaw of HAP.

Graphene oxide (GO) is a significant derivative of graphene possessing a two-dimensional lamellar structure formed by carbon atoms with  $\text{sp}^2$  hybridization [16–18]. Researchers pay attentions to GO on account of its outstanding characteristics, such as high electron mobility, large specific surface area, good electrical and strong mechanical properties [19–22]. GO lamellar structures are good barriers to the corrosive ions, oxygen and water [23]. The presence of surficial grafted functional groups (carboxyl, hydroxyl and epoxy groups etc.) facilitates the combination between GO sheets and epoxy resin system [24]. More importantly, the electrons collection ability of GO sheets can inhibit the electrons transfer during the whole corrosion reaction. Nonetheless, the acidity arising from carboxyls on GO sheets imposes adverse effect on

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protecting metallic substrates after a long immersion. Compositing GO with HAP is conducive to neutralize the acidity and achieve long-term anticorrosion behavior.

When the pH value of the system is greater than 3 (the isoelectric point of GO), the surface charge of the GO sheets presents negative, which reveals a facile electrostatic interaction with the metal ions [25]. Herein, in-situ bonding technology is proposed that  $\text{Ca}^{2+}$  ions bond with GO at first and then HAP nanoflakes in situ grow on GO sheets, forming graphene oxide-hydroxyapatite (GO-HAP) nanocomposite. The complicated interlaced structure of GO-HAP nanocomposite effectively impedes the penetration of corrosive species. The free  $\text{Cl}^-$  ions in the coating can be immobilized by the replacement with the rich hydroxyl groups in HAP to form more stable chlorapatite for reducing metallic destruction. The corrosion reaction is further restrained in the presence of GO by obstructing the cathodic half reaction. Therefore, the synergistic complementary protective effect of GO-HAP nanocomposite pigment can significantly enhance the corrosion resistance of epoxy resin system.

## 2. Experimental sections

### 2.1. Chemicals and materials

Anhydrous calcium chloride analytical reagent ( $\text{CaCl}_2$ , AR) and disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ , AR) were purchased from Shanghai Lingfeng Chemical Reagent Co., LTD. Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, AR) and graphite powders were obtained from Sinopharm Chemical Reagent Co., Ltd. GO was synthesized by Hummers method through exfoliation and oxidation processes of graphite powders. The epoxy varnish and polyamide hardener were provided by Changzhou Zhong Pu New Material Environmental Protection & Technology Co., Ltd. Mild steel panels of 40 mm × 10 mm × 5 mm acted as metal substrates polished by emery papers of 180–600 mesh. The chemical composition of the panels was listed in Table 1.

### 2.2. Fabrication of GO-HAP and HAP pigments

At first, a certain amount of GO (weight percent, wt % = 0.2, 0.6, 1.0%) was dispersed in 100 mL deionized water and then 0.025 mol  $\text{CaCl}_2$  powders was slowly added into GO solution (Scheme 1). 0.1 g EDTA-2Na as template were separately dissolved into the above suspension and 100 mL  $0.15 \text{ mol L}^{-1}$   $\text{Na}_2\text{HPO}_4$  solution. Under swift stirring and heating at 50 °C,  $\text{Na}_2\text{HPO}_4$  solution was instilled into  $\text{CaCl}_2$  solution with a speed of  $2 \text{ mL min}^{-1}$ . After that, anhydrous ethylenediamine was introduced into the mixture to adjust pH = 8. The mixture was continuously stirred for 20 min, and then aged at room temperature for 12 h. In the end, the prepared GO-HAP precipitates were washed by deionized water, and dried for 24 h in oven of 60 °C. The synthesizing process of HAP was similar to that of GO-HAP except for the addition of GO.

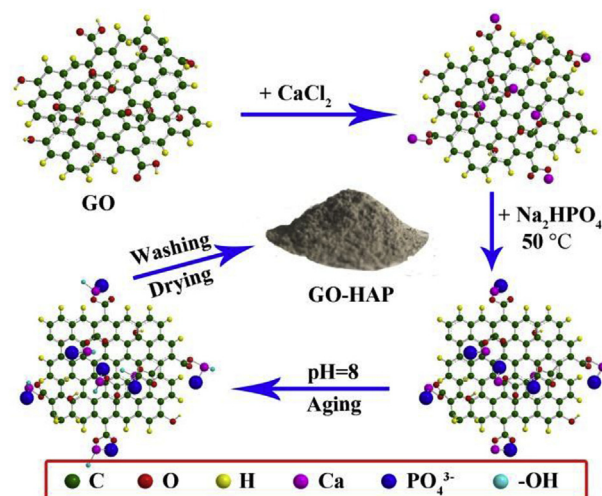
### 2.3. Preparation of anticorrosive coatings

First, 0.8 g anticorrosive pigment was introduced into 10 g epoxy resin varnish (60 wt %) and whisked for 1.5 h to ensure homodisperse. Then, 2 g polyurethane was diluted with equal amount of diluent to serve as curing agent, which was added into the above mixture and stirred for 30 min. After achieving homogenous deconcentration, the

**Table 1**

The chemical composition of the mild steel electrode.

Elements	Fe	C	Si	Mn	P	S	Cu	others
wt %	98.0	0.2	0.3	0.5	0.06	0.04	0.3	0.6



**Scheme 1.** Schematic of the preparation mechanism for GO-HAP nanocomposite.

commixture was sprayed onto the mild steel panels that were burnished by emery papers and cleaned by absolute ethyl alcohol beforehand. Finally, the coated mild steel panels were placed in drying oven at temperature of 50 °C and cured for one week.

### 2.4. Characterizations

X-ray powder diffraction (XRD, Shimadzu XD-3A, Cu K-radiation) and fourier transform infrared spectroscopy (FT-IR, Shimadzu IRPrestige-21) were used to study the crystal structures and composition of the pigment, respectively. Laser micro-Raman spectroscopy (Invia reflex) was carried out with a laser excitation of 514 nm to conform the presence of GO. Transmission electron microscopy (TEM, Hitachi S-4800) and scanning electron microscopy (SEM, Hitachi S-4800) were utilized to research the morphologies of the pigment. Energy Dispersive Spectrometer (EDS, Hitachi S-4800) was conducted to analyze elements mapping of the powders. X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK II) was measured to investigate the surface chemical constitution. Brunauer-Emmett-Teller measurement (BET, Micromeritics ASAP 2400) was performed to obtain the specific surface area of the pigments. The water contact angle (WCA, Dataphysics OCA35) was tested to discuss the water impermeability of the coatings.

### 2.5. Electrochemical experiments

The anticorrosion performance of the pigment was researched by electrochemical impedance spectroscopy (EIS, Zahner-Elektrok IM6e) experiment. The EIS experiment was conducted with a three-electrode system in 3.5 wt % NaCl solution [26]. The mild steel panels served as working electrode, saturated calomel electrode (SCE, CHI 150) as reference electrode and the platinum sheet (15 mm × 15 mm × 0.1 mm) as counter electrode. The EIS experiments were performed after immersion in NaCl solutions for 12, 24, 48 and 72 h, respectively. In the process of the measurements, the frequency scan range was  $10^{-1}$ – $10^5$  Hz, and the amplitude was 10 mV. And polarization curves were obtained at a sweep rate of 1 mV/s from  $-1.20 \text{ V}$  to  $-0.20 \text{ V}$ .

## 3. Results and discussion

### 3.1. Characterization of pigments

The crystal phase composition of the obtained samples is analyzed by X-ray diffraction (XRD). As shown in Fig. 1a, the pattern of HAP is

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