

Mass preparation and anticorrosion mechanism of highly triple-effective corrosion inhibition performance for co-modified zinc phosphate-based pigments

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ABSTRACT

The benzotriazole and GO co-modified zinc phosphate (ZP/BTA/GO) pigments with chemically oriented laminated structure are synthesized massively by in situ self-heating method for the first time. The heat released from the formation of ZP increases the solubility of BTA achieving the self-sufficiency of system energy in one step. After modification by BTA, the anticorrosive blind region of ZP pigments in the initial corrosion stage is repaired. With the co-modification by BTA and GO, the strong interaction among ZP, BTA and GO makes the compact laminated structure of ZP/BTA/GO pigments more stable, exerting bidirectional shielding effect on the penetration of corrosive medium. Meanwhile, the electrochemical impedance spectroscopy (EIS) and polarization curve tests reveal that the anticorrosion performance of ZP/BTA/GO pigments is increased by 366.1% compared to ZP pigments. The remarkable improvement of corrosion inhibition is attributed to the synergistic complementary anticorrosion mechanism containing the extension of electrons transport path, the deviation of electrons transfer and the formation of diversified passive films. The formation of zinc phosphate-based laminated pigments with full-covered anticorrosion time and excellent corrosion inhibition performance promotes the industrial production and development of anticorrosion materials.

1. Introduction

One effective and practical strategy for corrosion protection of metallic surfaces is application of different kinds of inhibitive pigments [1–3]. Although the environmentally friendly zinc phosphate (ZP) pigments are widely used anticorrosive pigments in industry [4–6], the anticorrosion activity is not satisfied due to their poor solubility and hydrolysis [7]. The anticorrosion effect of ZP pigments reflects that the released Zn^{2+} and PO_4^{3-} can connect with metal substrate forming complicate and compact passivating film to slow down the diffusion of corrosive ions [8,9]. However, the formation rate of passivating film appears delay, posing the anticorrosive blank area in the initial corrosion stage and limiting the wide application of ZP pigments [10,11]. Undesirable inhibitive performance of ZP directs our attention toward the modification of other alternatives based on ZP pigments.

To make up for the anticorrosive blank area of ZP pigments, the ZP is developed by several chemical or physical modifications [12–14]. The effective way on top of that is the recombination with organic

inhibitors [15]. One of the most attractive organic inhibitors is benzotriazole (BTA) molecules, they can form a dense protective barrier layer rapidly through the donor-acceptor reaction to protect metals from corrosion [16]. It prompts us to combine BTA with ZP to repair the deficiencies of ZP pigments, facilitating the prevention mechanism to take action faster. However, the poor solubility and stability of ZP/BTA pigments motivate us to covalently connect them with graphene oxide (GO). GO presents positive effect on metallic protection when it is introduced into the anticorrosive coatings [17,18], which is attributed to the electrons delocalization and collection ability [19–22]. The electrons produced by anodic corrosion reaction are attracted by GO, thus the cathodic reduction reaction is inhibited. Moreover, oxygen-containing functional groups on GO surface can combine with epoxy closely to form passivating film attaching to metal surface against the intrusion of corrosive species.

For promoting the development of anticorrosive pigments, for the first time, benzotriazole and GO co-modified zinc phosphate (ZP/BTA/GO) pigments are synthesized successfully following the in situ self-

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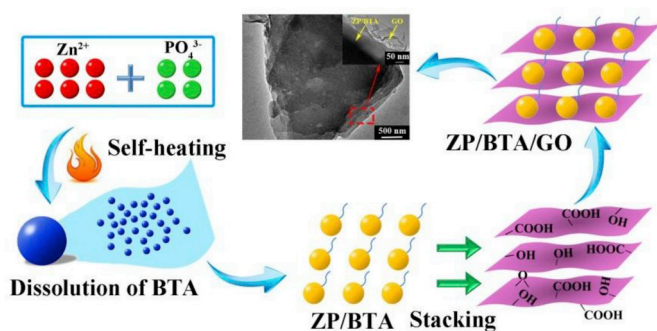
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Scheme 1. Synthetic schematic diagram of ZP/BTA/GO pigments.

Table 1

The chemical composition of the steel panels.

elements	Fe	C	Si	Mn	P	S	Cu	others
wt %	98.00	0.20	0.30	0.50	0.06	0.04	0.30	0.60

heating method. The essence is that the Zn–N bonds formed by the coordination of ZP with BTA, and the covalent Zn–O bonds formed by ZP load on GO sheets, thus generating the compact and stable laminated structure (Scheme 1). What is more, the heat released from the synthesis of ZP enhances the solubility of BTA, realizing the self-sufficiency of heat in one step and repairing the initial anticorrosion blank area of ZP pigments. The electron delocalization and mobility of GO induces the deflection of electrons transfer during corrosion. Finally, the influence on corrosion inhibition of ZP/BTA/GO pigments is analyzed by electrochemical impedance spectroscopy (EIS) and polarization curve tests, and the anticorrosive efficiency increases by 366.1% compared with ZP pigments. A triple-effective synergistic complementary mechanism of BTA and GO in ZP is proposed to explain the enhancement of anticorrosion performance. This work presents a simple industrialization production to broaden the practicability of ZP and other anticorrosive pigments.

2. Experimental sections

2.1. Reagents and materials

Zinc nitratehexhydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium phosphate (Na_3PO_4), and benzotriazole (BTA) were purchased from Tansoole Chemical Reagent Co., Ltd. (Shanghai, China). GO was fabricated by the

modified Hummers' method using graphite powder purchased from Sinopharm Chemical Reagent Co., Ltd. Epoxy resin and polyurethane curing agent were purchased from Changzhou Zhong Pu New Material Environmental Protection & Technology Co., Ltd. (Changzhou, China). All reagents were analytical grade and used as received.

2.2. Preparation of ZP/BTA/GO pigments

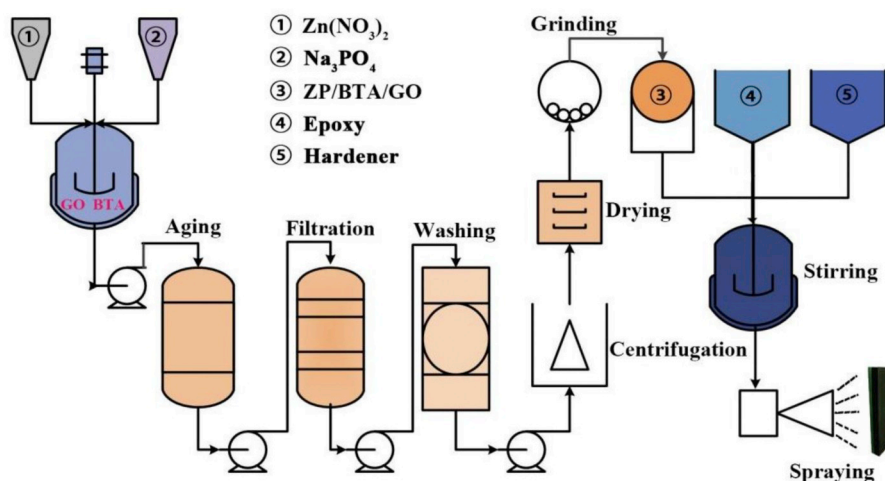
The ZP/BTA/GO pigments were synthesized in large quantities by in situ self-heating method with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Na_3PO_4 , BTA and GO. Firstly, 0.36 g BTA molecules and 2 mL of 8.70 mg/mL GO aqueous solution were dispersed homogeneously in 100 mL 0.08 mol/L Na_3PO_4 solution. Then 100 mL of 0.12 mol/L $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was dropped into the above Na_3PO_4 solution at a speed of 2 mL/min under ultrasonic condition for 2 h. After that, the suspension liquid was aged for another 2 h. Finally, the resulting ZP/BTA/GO pigments were washed by deionized water to remove the impurities and dried at 60 °C in the oven for 12 h. In the presence of corresponding materials, the synthesis of ZP pigments, ZP/BTA and ZP/GO pigments was similar with that of ZP/BTA/GO pigments.

2.3. Preparation of anticorrosive coatings

The anticorrosive coatings were coated on the clean and dry steel panels, of which chemical composition was displayed in Table 1 [23]. Before coating, the steels were polished with 100, 240, 600 meshes of SiC sand paper in turn, and rinsed with ethanol and acetone. The specific process for preparing anticorrosive coatings was as follows. 0.8 g as-prepared pigments were added into 10 g epoxy resin (60 wt %) to magnetic stirring strongly for 2 h obtaining homogeneous mixture. Afterwards, the mixture was added into 4 g curing agent (50 wt %) and stirred for another 1 h. Finally, the coatings were painted to the steel by a film applicator and weather at the room temperature for 5 days. The whole process was presented in Scheme 2.

2.4. Electrochemical corrosion measurement

Electrochemical impedance spectroscopy (EIS) and polarization curve tests were carried out by a three-electrode cell in the 3.5 wt % NaCl solution at room temperature at different immersion time for 6, 12, 24, 48 and 72 h. The three-electrode cell used in this experiment consisted of a platinum sheet auxiliary electrode, a Hg/Hg₂Cl₂ reference electrode, and metal substrate with coatings of 2.25 cm² work area as working electrode. When the electrochemical system reached the steady open voltage, the alternating-current (A.C.) impedance



Scheme 2. Schematic of macroscopic preparation of ZP/BTA/GO pigments and anticorrosive coatings.

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