ABSTRACT: The nanocomposite BTA-SiO$_2$-GO was fabricated for the purpose of metal corrosion protection. Herein, the BTA-loaded mesoporous silica nanocontainers were prepared through a facile one-step synthetic method. Subsequently, graphene oxide (GO) was combined with the resultant BTA-SiO$_2$ compound because GO had a superior barrier property and impermeability. We must note that the double functional groups exist on SiO$_2$. Benzotriazole (BTA), as an inhibitor, can be loaded into the nanocontainer and GO can also be modified by it, resulting in excellent dispersion in epoxy coatings, which were conducive to enhancing its anticorrosion performance. In this way, the nanocomposite endows the coating system with both self-healing and physical barrier abilities. The EIS results indicated that the impedance value of the BTA-SiO$_2$-GO composite coatings was up to $1.2 \times 10^9$ Ω cm$^2$, which indicated excellent corrosion resistant properties.

1. INTRODUCTION

Conventional coatings have failed to keep up with the demands of the increasingly important problem of metal corrosion in modern industry and daily life.$^1$ Intelligent coatings, which are generally composed of corrosion inhibitors and nanocontainers, are one of the most economical and widely used anticorrosion coatings, with a good pH response and self-healing ability.$^2,3$ The corrosion resistance of coatings depends largely on the ability of the loading corrosion inhibitor and controlled release ability of the corrosion inhibitor.$^4$ A variety of nanocontainers, including cyclodextrin, Elloit nanotubes, carbon nanotubes, metal–organic frameworks, zirconia, and mesoporous silica, have been reported, and mesoporous silica nanoparticles are a good example.$^5$ The excellent compatibility, high specific surface area, and large pore diameter have the advantages of good dispersion and strong load capacity. Mesoporous silica nanoparticles have the ability to respond to pH, which is commonly referred to as controlling the release of inhibitors. Moreover, its mechanical stability in the same type of material is also quite excellent.$^6,7$ It has been proven that a corrosion inhibitor can improve the corrosion resistance of coating through a number of studies. Nikpour et al. used *Urtica dioica* extract and GO to prepare anticorrosion coatings, but due to the complex and changeable corrosion environment, most of the extract would be released in advance, thus greatly reducing the anticorrosion efficiency.$^8$ Benzotriazole (BTA) derivatives are one of the most effective and commonly used corrosion inhibitors for metals. Sheng et al. synthesized a synergistic nanocomposite using the oxidation reaction of aniline and GO, but this material can only be passively anticorrosive and shows a lack pH responsiveness.$^9$ In this paper, mesoporous silica nanoparticles were synthesized to load BTA as smart coatings.$^{10−12}$

Because the solvent in the curing process of the coating under high temperature conditions results in evaporation at the same time the coating produces pores or cracks, a corrosive medium will therefore penetrate into the metal matrix, thereby damaging the coating. Therefore, the single self-healing property is not enough to prevent metal corrosion.$^{13}$ We prepared BTA-SiO$_2$-GO nanocomposites by doping GO to improve the physical barrier properties of the coating because of GO’s excellent barrier and impermeability. However, the poor dispersion of GO in epoxy coating will greatly affect the corrosion resistance of the coating. The dispersion in epoxy coatings can be enhanced by surface modification of GO due to its rich oxygen-containing functional groups on the surface.$^{14−17}$ It can be seen from the literature that the
modified GO surface greatly improves the dispersion of the epoxy coating and thus improves the corrosion resistance of the coating. Cao et al. used ethyl orthosilicate to modify GO, thereby improving the corrosion resistance.

2. EXPERIMENTAL SECTION

2.1. Materials. Graphite, phosphoric acid, sulfuric acid, sodium nitrate, hydrogen peroxide, potassium permanganate, tetraethyl orthosilicate (TEOS), benzotriazole (BTA), cetyltrimethylammonium bromide (CTAB), sodium hydroxide, 3-amino propyltrimethoxysilane (APTS), 3-glycidoxypropyltrimethoxysilane (GPTS), N,N-dimethylformamide (DMF), and ethanol came from Kelong Chemical Reagent Factory (Chengdu, China). The curing agent and epoxy resin were prepared by using the above methods.

2.2. Preparation of BTA-SiO$_2$ Nanocontainer. The mesoporous BTA-SiO$_2$ was synthesized by a facile one-step method. First, 0.21 g of sodium hydroxide was dissolved into 6101 mL of deionized water at 80 °C. Subsequently, 0.75 g of cetyltrimethylammonium bromide (CTAB), 1.25 g of benzotriazole (BTA), and 3.75 g of tetraethyl orthosilicate (TEOS) were added, and then the resultant was stirred for 2 h at 80 °C. Subsequently, the resultant was centrifuged at a rate of 6000 w/min. Finally, the mixture was washed with ethanol three times followed by vacuum drying at 90 °C in the oven for 6 h. The BTA-SiO$_2$ was fabricated.

2.3. Preparation of GO. GO nanosheets were prepared within the amended Hummer’s method. First, 100 mL of sulfuric acid (98%) and 1.8 g of graphite were put into an ice bath and stirred for 1.5 h. Then 8.8 g of KMnO$_4$ was added gradually to the resultant and stirred vigorously. Subsequently, the resultant was stirred for 24 h at room temperature. The mixture was watered down by addition of deionized water drop by drop, and then hydrogen peroxide was added to end the oxidation process. In the end, after centrifugation and washing by deionized water and vacuum drying at 60 °C for 24 h, the GO powder was prepared.

2.4. Modification of SiO$_2$. A 0.1 g portion of SiO$_2$ and 2 g of 3-aminopropyltriethoxysilane (APTS) were added to 90 g of ethanol, and ultrasonication was conducted. Then the resultant was stirred at 80 °C for 5 h. Meanwhile, 8 g of deionized water was slowly added. The resultant compound was centrifuged and washed (three times in pure water and three times in ethanol). Finally, the resultant was dried in a vacuum oven at 60 °C for 24 h.

2.5. Modification of GO. A 0.1 g portion of GO and 2 g of 3-glycidoxypropyltrimethoxysilane (GPTS) were added to 80 g of ethanol, and ultrasonication was conducted. After the mixture was stirred for 5 h at 80 °C, 8 g of deionized water was added. The mixture was centrifuged and washed (three times in pure water and three times in ethanol). In the last step, the obtained material was dried for 24 h in a 60 °C oven to obtain f-GO.

2.6. Preparation of BTA-SiO$_2$-GO Composite. A 250 mg of f-GO was added to 100 mL of DMF, and ultrasonication was conducted for 15 min. Then 50 mg of f-SiO$_2$ was added to the above solution, and ultrasonication was conducted for 15 min. The solution was stirred at 105 °C for 6 h. The resultant mixture was centrifuged and washed (three times in pure water and three times in ethanol).

2.7. Preparation of Composite Coatings. The coating was obtained by the following method. First, 5 mL of (10 mg/mL) of BTA-SiO$_2$ aqueous was mixed with 1.8 g of curing agent. The compound was stirred for 30 min, followed by 30 min of ultrasonic treatment. In order to ensure that the BTA-SiO$_2$ composite material has good dispersion in the coating, after the excess solvent was removed by centrifugation, 2 g of epoxy resin was added and the mixture stirred for 30 min. Subsequently, the mixture was put through the degassing step in a vacuum oven for 10 min at ambient temperature. Finally, the composite was coated with a brush to a thickness of about 100 μm on the pretreated carbon steel. The coated carbon steel was cured at room temperature for 48 h and then cured for 12 h in a 120 °C oven. The coating was named BTA-SiO$_2$/EP. Pure epoxy coating and BTA-SiO$_2$-GO/EP coating were prepared by using the above methods.

2.8. Instruments and Characterization. A WQF-520 infrared spectrometer (Beijing Rayleigh Analytical Instrument Co., Ltd.) was used for Fourier transform infrared spectroscopy analysis. The crystalline structures of these composites were investigated using an X-ray diffractometer (PANalytical, Panalytical, etc.)
3. RESULTS AND DISCUSSION

3.1. Material Characterization and Assessment.

3.1.1. Infrared Spectrum (FTIR) Analyses. Figure 1 shows the FTIR of SiO₂, f-SiO₂, GO, f-GO, and SiO₂-GO. As for SiO₂, a wide peak was detected at 3380 cm⁻¹ which was due to the O–H stretching. Compared with SiO₂, the C–H stretching peaks obtained at 2935 and 2878 cm⁻¹ and the N–H peak detected at 814 cm⁻¹ of f-SiO₂ were attributed to the amendment of APTS. The peak at 1109 cm⁻¹ represented Si–O–Si bonding. These results indicated the successful combination between GO and SiO₂.

3.1.2. X-ray Diffraction (XRD) Tests. The characteristic diffraction peak of SiO₂ appears at 21° and is a wide peak, which proves that SiO₂ has been successfully prepared. As for GO, the characteristic diffraction peak appeared at 9.8°. As for SiO₂-GO, the broad peak at 21° could be observed as well. In addition, the GO characteristic diffraction peak at 9.8° almost disappeared. These observations demonstrated the successful combination between GO and SiO₂.

3.1.3. Thermostability Analyses. TGA measurements were performed to estimate the BTA loading capacity of the nanocontainers. The weight losses for SiO₂, CTAB-SiO₂, and BTA-CTAB-SiO₂ are displayed in Figure 3. In the first stage (below 100 °C), about 3% weight loss for three composites.
could be observed, which was due to the adsorbed moisture in powder. SiO$_2$ has little weight loss, which proves SiO$_2$ has good thermal stability. When CTAB is decomposed at 200–300 °C, the weight loss of CTAB-SiO$_2$ is about 18%. As for BTA-CTAB-SiO$_2$, about 47% weight loss can be observed at 100–300 °C; the first stage (begin at 100 °C) was ascribed to the decomposition of BTA, while the second stage (begin at 200 °C) was attributed to the decomposition of CTAB. According to the comparison, it is clear that the encapsulation amount of BTA was about 29%. From the above results, it can be concluded that SiO$_2$ nanocontainers are successfully loaded with BTA corrosion inhibitor.

3.1.4. Release of BTA Inhibitor. The release of a corrosion inhibitor from the nanovessel was experimentally verified by UV−vis spectrophotometry. The absorbance intensity of BTA was recorded in 3.5 wt % NaCl suspension containing BTA-SiO$_2$ with different conditions (pH = 3, 7, and 11). Figure 4 shows two stages of BTA release: rapid release and gradual release. Apparently, under different pH conditions, the release rate of BTA is different, indicating that the release progression is pH responsive. At pH 3, BTA was almost completely released for just 5 h, implying the speedy release rate and the hugest release amount. At pH 7 and 11, the initial stage lasted for 12 h, which was ascribed to a slow release rate. In addition, the release amount decreased a lot.

3.1.5. BET Experiments. As can be seen in Figure 5a, nitrogen adsorption/desorption results of SiO$_2$ are of typical type IV (based on IUPAC definition) with a hysteresis loop in the P/P$_0$ region of 0.45−0.95. This can be ascribed to the instability of liquid N$_2$ in the narrow channels, indicating the presence of a mesoporous material, confirming the successful fabrication of mesoporous SiO$_2$. As for BTA-SiO$_2$, the hysteresis loop disappeared, which indicated that the loading of BTA and CTAB nanoparticles occupied the mesoporous material, confirming the successful loading of BTA into SiO$_2$. Also, this can be proved by the pore size distribution of the two samples. As can be seen from Figure 5b, the average pore size of SiO$_2$ was about 16.03 nm. After the loading of BTA, the average pore size was decreased to 5.91 nm. These results proved the prosperous loading of BTA into SiO$_2$.

3.1.6. XPS Analyses. The composition of BTA-SiO$_2$-GO nanocomposites can be expressed by XPS tests, and these results are presented in Figure 6. It can be seen from Figure 6a that C, N, O, and Si elements exist in the composite material. Apparently, in Figure 6d, the peak of the Si−O−Si binding energy is 531.98 eV, and in Figure 6e, the peak of the O−Si−O binding energy is about 102.17 eV, indicating the successful synthesis of SiO$_2$. In addition, the peaks of binding energies of 284.81, 286.06, 288.32, and 399.55 eV represent C−C/C=C, C−O/C=N, C=C, and N−H, respectively, while the C=C=C=C, C=O/C=O were ascribed to the GO and the silane coupling agent (APTS/GPTS) and the −N−H was ascribed to the amido bond of the combination of f-SiO$_2$ and f-GO. These results showed that the BTA-SiO$_2$-GO nanocomposite was fabricated successfully.

3.1.7. Raman Test. Figure 7 displayed the Raman spectra of GO and SiO$_2$-GO. As expected, the samples displayed the typical lower intensity D band at 1360 cm$^{-1}$ along with a G band at 1595 cm$^{-1}$. The D band represents a defect in the lattice of carbon atoms, and the G band represents sp$^2$ hybridization of carbon atoms for in-plane stretching vibration. The $I_D/I_G$ ratio of GO was 0.95, while the $I_D/I_G$ ratio of SiO$_2$-GO was 0.82. The decrease demonstrated that the SiO$_2$
particles had replaced the carbon atoms and anchored onto the GO surface, indicating the successful combination of SiO$_2$ and GO.

3.1.8. Morphological Studies. SEM analyses were carried out to explore the morphology of BTA-SiO$_2$ and BTA-SiO$_2$-GO. Figure 8a1 displays the morphology of BTA-SiO$_2$, which are spherical particles in different shapes. As shown in Figure 8b1, the BTA-SiO$_2$-GO particles show a smaller size and better dispersibility. Additionally, it can be observed that the BTA-SiO$_2$ particles were loaded on GO. Moreover, the mapping of EDS analysis proved the presence of N and Si elements, proving the merging of BTA and SiO$_2$. These consequences showed that two nanocomposites were made up well.

3.2. Characterization of Coatings. 3.2.1. Section Results of Coating. Scanning electron microscopy (SEM) was used to observe the fractured surface of the coating to verify the compatibility and dispersity between the prepared nanocomposites and the resin. Surfaces without added composites are smooth and shiny. However, there were some micropores (red circle). As for GO/EP coating, obvious agglomeration and layers stacked could be observed, which was attributed to the strong van der Waals forces. There were a lot of aggregations in BTA-SiO$_2$/EP coating, implying the weak dispersion. As for BTA-SiO$_2$-GO/EP coating, the aggregation phenomenon was apparently reduced, which was attributed to the modification of SiO$_2$ to GO, resulting in the excellent compatibility between BTA-SiO$_2$-GO and the epoxy resin.

3.3.1. Electrochemical Impedance Spectroscopy Analyses. In general, the corrosion process of a coating is always composed of the following two stages. Usually, an EIS measurement method is used to test and evaluate the anticorrosion performance of nanocomposite coatings with different proportions under different immersion time. EIS measurement results and equivalent circuits are shown in Figure 10. In the first stage, the corrosive substance moves away from the metal matrix and is represented by a time constant. In the second period, the corrosive material has entered the coating and penetrates the coating into contact.
with metal matrix and begins the corrosion progression, communicated by the second time constants. 38−41

Nyquist plots are shown in Figure 10a. The impedance modulus of pure EP coating decreased dramatically from $7.12 \times 10^8$ to $3.81 \times 10^8$ $\Omega$ cm$^2$ after a 7 day immersion process. The impedance modulus decreased to $2.0 \times 10^8$ $\Omega$ cm$^2$ after 15 days of immersion and further decreased to $5 \times 10^7$ $\Omega$ cm$^2$ after 30 days. The appearance of two impedance arcs means that the time constant becomes two. The pure EP coating has micropores or microcracks, resulting in poor barrier performance (Figure 9a). The GO/EP coating accelerates the corrosion behavior of the matrix. When GO is added into the epoxy resin, the agglomeration phenomenon (Figure 9b)
results in poor dispersion. EIS measurements showed that the impedance decreased faster than pure EP coating. In contrast, the impedance of the BTA-SiO$_2$/EP coating is $8.3 \times 10^8$ Ω cm$^2$ at the initial immersion stage. Due to the active inhibition properties of the BTA-SiO$_2$/EP coating, the impedance of coating increased significantly at 15 days. Meanwhile, the slow decline of impedance modulus of the coating can also be attributed to its active inhibition performance. The impedance modulus of BTA-SiO$_2$-GO/EP coating is further increased to $1.3 \times 10^9$ Ω cm$^2$ at the beginning of the soak. GO has a physical barrier, and BTA-SiO$_2$-GO nanocomposites are evenly dispersed in epoxy coating. In addition, the active suppression performance of the coating is better reflected in that the

Figure 10. Bode and Nyquist plots of (a) pure EP, (b) GO/EP, (c) BTA-SiO$_2$/EP, and (d) BTA-SiO$_2$-GO/EP coatings at different immersion times in 3.5 wt % NaCl solution. (e) The corresponding equivalent electric circuit.
Figure 11. Bode and Nyquist plots of (a) pure EP, (b) GO/EP, (c) BTA-SiO$_2$/EP, and (d) BTA-SiO$_2$-GO/EP coatings at different immersion times under acidic conditions (pH = 3). (e) Corresponding equivalent electric circuit.
impedance modulus of the 15th and 30th day is higher than that at the seventh day. In addition, it is shown from the Bode diagram (Figure 10b) that the change of impedance modulus of EP coating at $Z_\text{r}$ = 0.01 Hz is related to the change of immersion time. Different from pure EP coating, the impedance of BTA-SiO$_2$-EP and BTA-SiO$_2$-GO/EP coatings rebound in numerical value, which is a manifestation of the proactive inhibition presentation of BTA-SiO$_2$-EP coatings. According to the bode phase angle diagram of the pure EP coating (Figure 10c), the maximum value of the low-frequency region indicates that the barrier has weak anticorrosion presentation, which is consistent with the results of Figure 10a1. The change of breakpoint frequency can reflect the coating inhibiting the diffusion of corrosive media. Among the increase of immersion time, the breakpoint frequency ($f_b$) increases, which proves that the corrosive medium has spread to the surface of the metal matrix. With the extension of immersion time, the phase Angle values of BTA-SiO$_2$-EP coating and BTA-SiO$_2$-GO/EP coating at 10 kHz show a difference. Compared with the coating containing GO, the coating without GO shows a downward trend, and the breakpoint frequency also increases. This may be due to the difference caused by GO outstanding barrier properties. In summary, the corrosion resistance of the prepared BTA-SiO$_2$-GO/EP coating can be ascribed to the following reasons:

Corrosion inhibition ability of BTA, active release of corrosion inhibitor by SiO$_2$, and strong physical barrier of GO.

3.3.2. Electrochemical Analysis under Acidic Conditions. In order to ensure the pH of the solution (pH = 3), HCl is added to the 3.5 wt % NaCl solution. As shown in the Nyquist diagram (Figure 11a), for the EP coating, the impedance modulus cut severely from 2.21 × 10$^8$ to 2.57 × 10$^7$ Ω cm$^2$ after 7 days immersion in acid solution (pH = 3). After 15 days of soaking, the impedance was reduced to 8.74 × 10$^6$ Ω cm$^2$. This result is caused by the micropores and cracks in the pure EP coating itself. An acidic environment will accelerate corrosion. In pH = 3 solution, the GO/EP coating appears to have worse corrosion resistance, which is reflected in the impedance spectrum as the impedance modulus decreases more rapidly (from 3.25 × 10$^8$ to 2.02 × 10$^7$ Ω cm$^2$) than the EP coating behind soaking for the equal time. Because of GO agglomeration, the corrosion of the metal matrix was accelerated. In addition, an acidic environment will accelerate corrosion. For BTA-SiO$_2$/EP coating, the initial value of impedance modulus reaches 9.13 × 10$^6$ Ω cm$^2$, and the impedance modulus decreases slowly with the extension of immersion time. The active release of BTA in the BTA-SiO$_2$/EP coating made the impedance on the 15th day better than the 7th day. The impedance of BTA-SiO$_2$-GO/EP coating is further enlarged to 3.61 × 10$^8$ Ω cm$^2$ at the initial stage of soaking in acidic solution of pH = 3. This result is caused by the combined effect of the barrier of GO to corrosive media and the better dispersion of BTA-SiO$_2$-GO composite nanomaterials resin. The impedance of BTA-SiO$_2$-EP and BTA-SiO$_2$-GO/EP after immersion for 7 days decreases slower than that of pure EP and GO/EP due to the increase in the release rate of BTA under acidic conditions.

The impedance of pure EP weakens with the delay of soaking time near the ground frequency ($Z_\text{r}$ = 0.01 Hz) of the bode-frequency diagram (Figure 11b). The impedance modulus rebound of the coatings containing BTA was observed, indicating that BTA can inhibit corrosion and increase the release rate under acidic conditions. Above and beyond, the change of the breakpoint frequency ($f_b$) and the phase angle values again proves that the hurdle of coating is not adequate to keep the corrosive medium away from the metal substrate. The breakpoint frequency of BTA-SiO$_2$-GO/EP composite coating hardly changes, which could be owed to the marvelous barrier property of GO. In summary, BTA-SiO$_2$-GO/EP coatings show brilliant corrosion resistance. This is ascribed to the amazing corrosion inhibition property in acid solution (pH = 3) and the superior control release ability of SiO$_2$ and admirable physical obstacle presentation of GO.

3.4. Schematic of the Active Inhibition Mechanism. It is known that the curing process can initiate micropores and cracks in the coating, which is ascribed to the solvent’s evaporation. It is because of their presence that the corrosive medium is able to contact the metal matrix and cause corrosion. Under these conditions, the homodispersion of BTA-SiO$_2$-GO will become a physical barrier in restricting the corrosive mediums penetrating into the metal substrate at first, which greatly prolongs the corrosion path and the corrosion time. More importantly, metal corrosion is always accompanied by electrochemical corrosion, which will cause the pH value change. While the pH value changes, the BTA molecules can release from SiO$_2$ nanocounters and adsorb on the corrosion area to put their corrosion inhibition property to good use. The illustration of the active inhibition mechanism is shown as Figure 12, which vividly reveals the outstanding barrier property and impermeability of GO and the active inhibition of BTA.
fabricated in the work shows enormous potential for applications for metal corrosion protection.

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**Notes**

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