

Long-lasting corrosion protection of rusted steel via TA-driven chemical modification of LDH-diatomite and adsorption of 8-hydroxyquinoline

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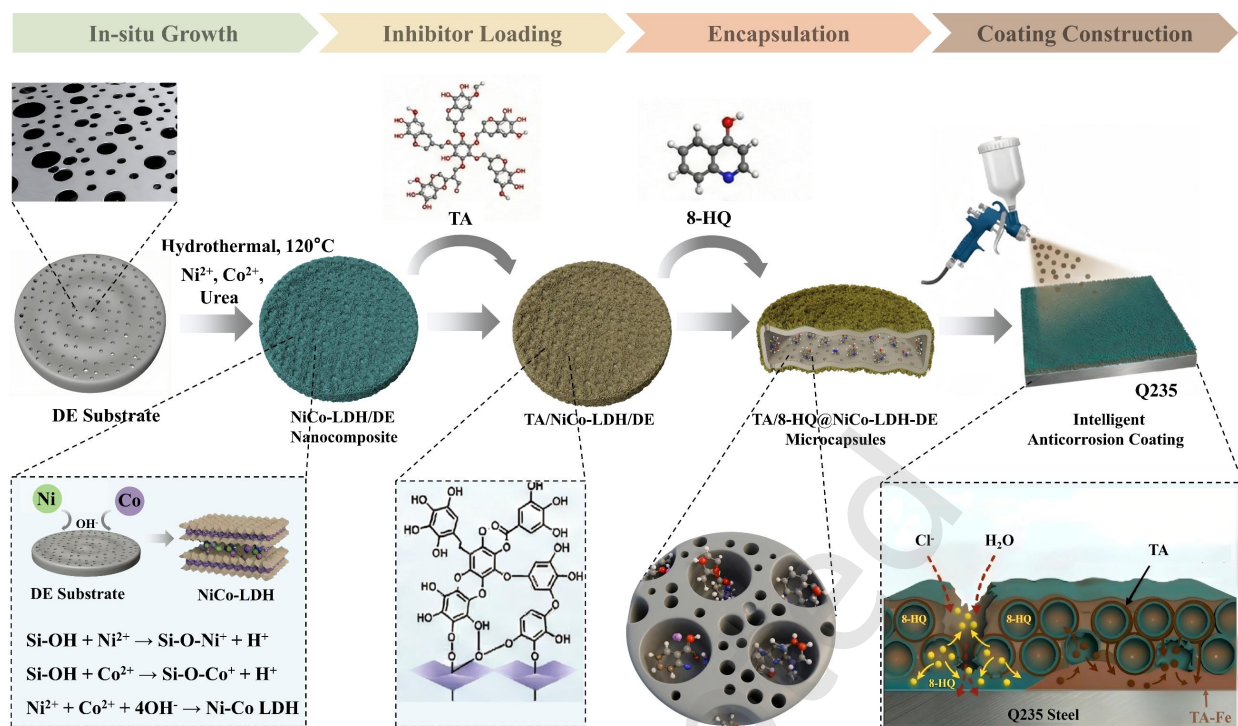
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The Figure shows the synthesis process of TA/8-HQ@LDH-DE fillers, the spraying operation on the surface of Q235 carbon steel, and the reaction process between the ruptured microcapsules and rusts.

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ABSTRACT: Steel corrosion in humid and saline environments severely threatens infrastructure service durability, while traditional coatings exhibit poor adhesion to rusted steel substrates. Herein, we fabricate a multifunctional anticorrosive filler via facile co-precipitation to in-situ grow Ni-Co layered double hydroxides (LDH) on diatomite (DE). Tannic acid (TA) acts dually as an efficient rust converter that converts iron oxides into stable iron tannate complexes, and a nucleation regulator for homogeneous LDH growth. The corrosion inhibitor 8-hydroxyquinoline (8-HQ) is anchored onto the LDH-DE skeleton via weak electrostatic and coordination interactions, achieving stimuli-responsive sustained release in corrosive media. When embedded into EP resin, the prepared TA/8-HQ@LDH-DE filler realizes hierarchical anticorrosion effects: physical barrier blocking ion penetration, in-situ rust conversion at steel coating interface, and stimuli-responsive inhibitor release to passivate active corrosion sites. Combined electrochemical impedance spectroscopy (EIS) tests and molecular dynamics simulations verify its outstanding anticorrosion performance on rusted Q235 steel. Notably, the TA/8-HQ@LDH-DE/EP coating containing 20 wt.% filler maintained the $|Z|_{0.01\text{Hz}}$ value of $4.52 \times 10^8 \Omega \cdot \text{cm}^2$ after 40 days of immersion, approximately two orders of magnitude higher than that of the EP coating. This work provides a scalable strategy for integrating passive barrier protection, interfacial rust stabilization, and active intelligent anticorrosion functions toward durable protection of rusted steel substrates.

KEYWORDS: rust conversion coating; controlled corrosion inhibition; synergistic anti-corrosion; diatomite microcapsule; tannic acid modification; 8-HQ corrosion inhibitor

1 Instructions

Steel is widely used for its high performance and low cost but is prone to corrosion in humid and saline environments [1-3]. Chloride ions and moisture penetrate the steel surface, triggering electrochemical dissolution that progressively undermines structural integrity [4-6]. On rusted steel, the porous and loosely adherent rust layer not only weakens the interfacial adhesion between the coating and the substrate, but also creates localized micro-environments that accelerate further corrosion beneath the coating [7-12]. Conventional protective coatings, including widely used epoxy systems, act primarily as physical barriers against the ingress of corrosive ions and moisture, and perform well on clean steel surfaces [13-15]. However, they fundamentally fail on pre-corroded surfaces because they lack the ability to chemically stabilize the underlying rust layer, leading to premature delamination and coating breakdown [16-18]. Rust converters such as tannic acid (TA) can chelate iron ions to stabilize rust and improve adhesion [19-22].

However, their rapid consumption limits long-lasting corrosion protection. To address this limitation, active corrosion protection strategies incorporating smart nanocontainers capable of on-demand inhibitor release have emerged as a promising approach [23].

Layered double hydroxides (LDHs) have attracted considerable attention in corrosion protection owing to their unique two-dimensional layered structure, tunable chemical composition, and large specific surface area, which enable efficient intercalation, storage, and controlled release of corrosion inhibitors. Moreover, the positively charged hydroxide layers and exchangeable interlayer anions endow LDHs with excellent ion-exchange capability, allowing them to actively capture aggressive chloride ions and release protective species in response to corrosive environments. These characteristics make LDHs ideal nanocontainers for the construction of smart self-healing anti-corrosion systems [24-26].

Diatomite (DE), a naturally abundant biogenic silica

material, has emerged as an attractive support for multifunctional anti-corrosion fillers due to its highly porous hierarchical architecture, excellent mechanical stability, low density, and abundant surface hydroxyl groups. The hollow cavity structure of DE not only provides additional loading sites for functional molecules but also facilitates the efficient encapsulation and sustained release of active species, thereby enhancing the overall protective performance and long-term durability of composite coatings [27-29].

In-situ growth of Ni-Co LDH nanosheets on DE yields a stable hierarchical structure, which provides abundant active sites for subsequent modification and corrosion inhibitor loading [30-32]. TA can coordinate with metal ions on the LDH surface, improving interfacial compatibility, and converts unstable rust into stable and dense complexes, achieving passivation and stabilization of corrosion products [33]. Loading the fluorescent corrosion inhibitor 8-hydroxyquinoline (8-HQ) into the interlayers of LDH-DE endows the system with controlled-release capability, allowing sustained release of the inhibitor in the local microenvironment of the coating, effectively inhibiting corrosion propagation and enhancing the active anti-corrosion performance of the coating system [34-36].

This work introduces a novel multifunctional anticorrosion filler, which is prepared as follows: LDH nanosheets were grown in situ on DE, functionalized with TA for rust conversion, and loaded with 8-HQ as a corrosion inhibitor. The hybrid filler (TA/8-HQ@LDH-DE) was incorporated into epoxy resin to prepare composite coatings that can be directly sprayed onto rusted Q235 carbon steel. This design combines passive barrier protection and active corrosion protection: the lamellar LDH and porous DE form a compact barrier, while TA achieves rust conversion and 8-HQ provides sustained release, greatly improving the long-term anticorrosion performance. The method is simple and suitable for large-area spraying, offering an innovative strategy for the protection of rusted steel. Systematic studies on the structure-performance relationship and corrosion mechanism are essential to promote its practical engineering applications.

2 Experimental

2.1 Materials

Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were purchased from Shanghai Aladdin Reagent Co., Ltd. Urea ($\text{CO}(\text{NH}_2)_2$), ethanol and ethyl acetate were bought from Chongqing Huanghui Chemical Hazardous Materials Sales Co., Ltd. 8-

hydroxyquinoline (8-HQ) and (TA) were obtained from Shanghai Maclin Biochemical Technology Co., Ltd. Epoxy resin and curing agent were purchased from Wuxi Qiangguang Chemical Raw Materials Co., Ltd. Q235 steel substrates ($8 \times 8 \times 2$ mm) were purchased from Deno Steel. Deionized water was prepared in the laboratory.

2.2 Preparation of active fillers

2.2.1 Preparation of LDH-DE filler

For the synthesis of LDH-DE, 0.519 g NH_4F and 0.432 g urea were first dissolved in 60 mL of deionized water under magnetic stirring to form a homogeneous solution. Subsequently, 0.058 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.174 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 0.06 g DE were sequentially introduced, followed by continuous stirring for 30 min to obtain a uniformly dispersed precursor suspension. The suspension was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 120°C for 12 h in a hydrothermal reactor, during which Ni-Co LDH nanosheets were in situ grown on the DE surface. After naturally cooling to room temperature, the product was collected for subsequent purification and drying. To ensure sample consistency and reproducibility, the synthesis was repeated several times under identical conditions to obtain sufficient material for further characterization and coating preparation.

2.2.2 Preparation of TA/LDH-DE filler

The TA/LDH-DE composite was prepared by surface functionalization of the as-prepared LDH-DE with TA. Specifically, 2.5 g of TA was dissolved in 50 mL of deionized water under magnetic stirring in a 50°C water bath until a clear solution was obtained. A 1 mol/L NaOH solution was then slowly added dropwise to adjust the pH of the solution to 4-6. Subsequently, 3-4 g of the pre-synthesized LDH-DE composite was added, and the mixture was stirred at 40°C for 4 h to ensure sufficient TA loading and surface modification. After the reaction, the product was separated, washed, and dried to obtain the TA/LDH-DE composite.

2.2.3 Preparation of TA/8-HQ@LDH-DE filler

The TA/8-HQ@LDH-DE composite was prepared by using the as-synthesized TA/LDH-DE as the carrier via an adsorption-assisted loading method. Typically, equal masses of 8-HQ and TA/LDH-DE (0.5-1.0 g each, depending on the target yield) were dispersed in 50-100 mL of distilled water under magnetic stirring for 30-60 min to form a homogeneous suspension. The suspension was subsequently ultrasonicated for 10-15 min to enhance dispersion and promote the loading of 8-HQ into the porous TA/LDH-DE structure. The resulting suspension was then transferred to

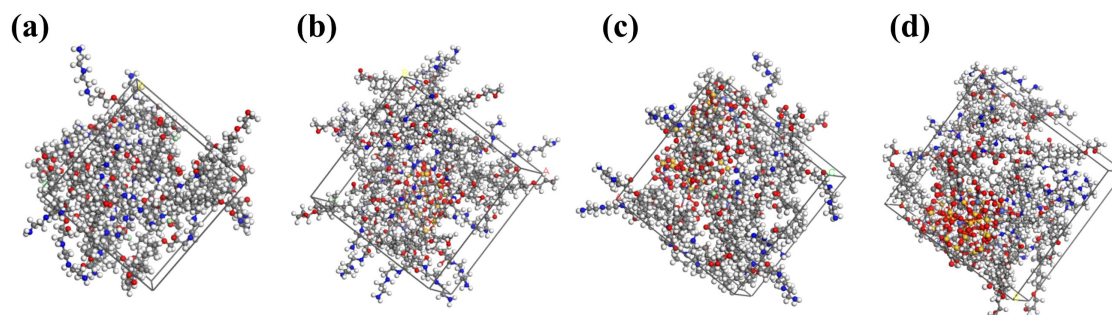


Fig. 1 MD modeling of (a) EP, (b) LDH-DE/EP, (c) 8-HQ@LDH-DE/EP and (d) TA/8-HQ@LDH-DE/EP.

a vacuum drying oven and dried at 60 °C under -0.08 MPa for 12 h, allowing solvent removal and effective immobilization of 8-HQ within the TA/LDH-DE carrier. After drying, the system was slowly returned to atmospheric pressure and allowed to stand for 1 h to stabilize the composite structure and minimize structural damage caused by rapid pressure release. The obtained solid was then gently ground to reduce agglomeration and stored in a dry environment for subsequent use, denoted as TA/8-HQ@LDH-DE.

2.2.4 Preparation of composite coatings

Pre-rusted Q235 carbon steel was used as the substrate. To simulate rusted-surface coating conditions, the substrate was subjected only to simple mechanical surface treatment. Specifically, the surface was sequentially ground with 600, 800, and 1000 grit silicon carbide sandpapers to remove loosely adhered rust layers and surface contaminants while retaining the firmly bonded residual rust layer. The treated specimens were then ultrasonically cleaned in absolute ethanol and preheated at 120 °C prior to coating application. For the preparation of the EP coating solution, 1.5 g of E51 EP resin and 1.5 g of curing agent were dissolved in 15 mL of ethyl acetate to obtain the EP base solution. The resulting solution was directly applied onto the mechanically treated rusted Q235 carbon steel surface by high-pressure spraying, followed by curing at 150 °C for 2 h to obtain the pure EP coating. The curing temperature (150 °C, 2 h) was selected to ensure complete crosslinking of the epoxy coating and does not induce significant phase transformation of the pre-rusted layer during the relatively short curing period. For the preparation of the composite coatings, 0.30 g, 0.60 g, and 1.20 g of functional fillers (LDH-DE, TA/LDH-DE, or TA/8-HQ@LDH-DE) were separately added into the above EP base solution. After sufficient dispersion, the mixtures were directly spray-applied onto the rusted steel surface using the same spraying and curing conditions as those for the pure

EP coating. During sample preparation, all coatings were fabricated under identical spraying conditions, including the same substrate preparation procedure, spraying distance, coating passes, and curing conditions, to minimize the influence of thickness variation on the anti-corrosion comparison. As shown in Fig S2, the average thicknesses of pure EP, 10 wt.%, 20 wt.%, and 40 wt.% TA/8-HQ@LDH-DE/EP coatings were approximately 117, 118, 119, and 123 μm , respectively. All coatings exhibited comparable thicknesses within the range of approximately 117–125 μm , indicating that the thickness variation among different groups was limited. Therefore, the differences in anti-corrosion performance among various coatings can be mainly attributed to the contribution of the TA/8-HQ@LDH-DE filler rather than the variation in coating thickness. The obtained composite coating samples were denoted as LDH-DE/EP, TA/LDH-DE/EP, and TA/8-HQ@LDH-DE/EP, respectively.

2.3 Simulation of barrier properties

Molecular dynamics (MD) simulations were performed using Materials Studio to evaluate the barrier performance of the TA/8-HQ@LDH-DE/EP composite coating. The amorphous coating models were constructed using the Amorphous Cell module, and periodic boundary conditions were applied in all three spatial directions [37–39]. All models were built in orthorhombic simulation cells, with the lattice angles fixed at $\alpha = \beta = \gamma = 90^\circ$, to ensure consistency in structural construction and improve the reliability and comparability of the simulation results, as schematically illustrated in Fig. 1. Fig. 1 shows the schematic diagram of the MD simulation models for EP, LDH-DE/EP, 8-HQ@LDH-DE/EP, and TA/8-HQ@LDH-DE/EP.

Four coating models with different compositions were established for comparative MD simulations: (i) a pure EP model ($24.9 \times 24.9 \times 24.9 \text{ \AA}^3$), containing 20 EP molecules, 3

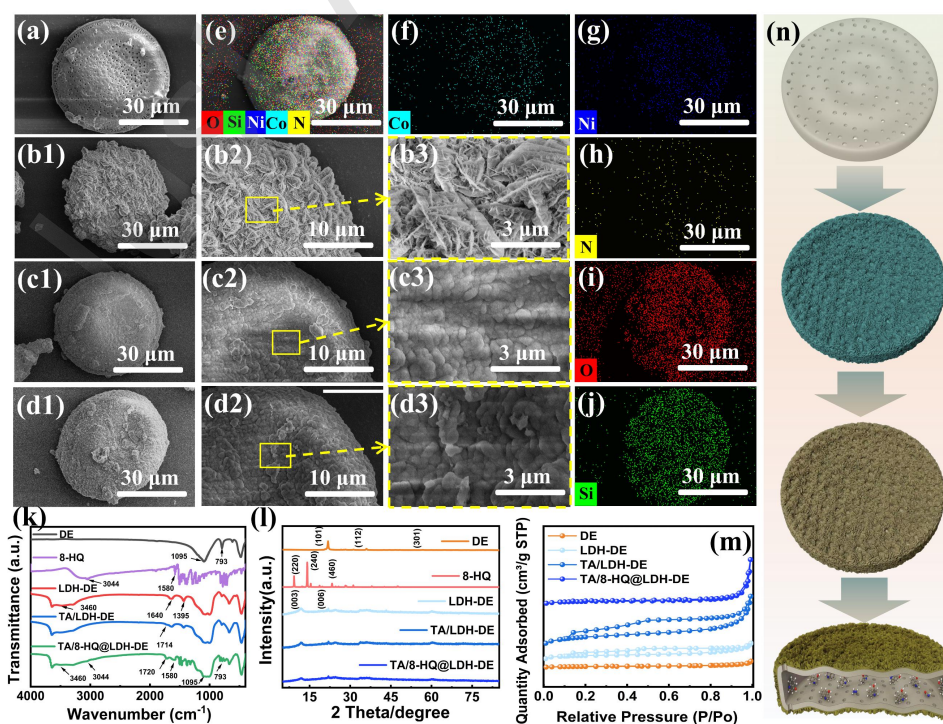


Fig. 2 SEM images: (a) DE, (b1-b3) LDH-DE, (c1-c3) TA/LDH-DE, (d1-d3) TA/8-HQ@LDH-DE; (e-j) EDS pattern of TA/8-HQ@LDH-DE; (k) and (l) FTIR and XRD diffraction peaks of DE, 8-HQ, LDH-DE, TA/LDH-DE, and TA/8-HQ@LDH-DE; (m) N₂ adsorption/desorption isotherms of DE, LDH-DE, TA/LDH-DE and TA/8-HQ@LDH-DE; (n) Schematic diagram of the synthesis of TA/8-HQ@LDH-DE material.

Cl⁻, 3 H₂O molecules, and 1 O₂ molecule; (ii) an LDH-DE/EP model (26.5×26.5×26.5 Å³), consisting of 18 EP molecules, 2 LDH-DE units, 3 Cl⁻, 3 H₂O molecules, and 1 O₂ molecule; (iii) TA/LDH-DE/EP model (27.2×27.2×27.2 Å³), consisting of 18 EP molecules, 2 TA/LDH-DE units, 3 Cl⁻, 3 H₂O molecules, and 1 O₂ molecule; and (iv) a TA/8-HQ@LDH-DE/EP model (26.2×26.2×26.2 Å³), consisting of 18 EP molecules, 2 TA/8-HQ@LDH-DE units, 3 Cl⁻, 3 H₂O molecules, and 1 O₂ molecule. By comparing the diffusion behavior of aggressive species in these systems, the role of functional fillers in regulating the barrier performance of the EP coating can be systematically revealed.

To ensure direct comparability among the simulation systems, all coating models were constructed with the same number of aggressive species, namely 3 Cl^- , 3 H_2O molecules, and 1 O_2 molecule. Prior to the formal MD simulations, energy minimization was performed for all models to eliminate unfavorable contacts in the initial configurations and relieve internal stress within the systems. The structural optimization was carried out using the Smart Minimizer algorithm in combination with the conjugate gradient method to ensure adequate energy convergence. Subsequently, MD simulations were performed in the NPT ensemble at 298 K and 1 atm using the COMPASS II force

equilibrium, each model was equilibrated under NPT conditions for 300 ps. After equilibration, the barrier performance and anticorrosion mechanism of the different coating systems were evaluated by analyzing the mean square displacement (MSD) of aggressive species (H_2O , O_2 , and Cl^-) within the coating matrix, together with the fractional free volume (FFV) of the coatings. These analyses provide molecular-scale insights into the enhanced barrier effect imparted by the TA/8-HQ@LDH-DE filler in the EP coating.

2.4 Characterization of the active filler

Fourier transform infrared spectroscopy (FTIR) was employed to analyze the changes in functional group structures of DE, 8-HQ, LDH-DE, TA/LDH-DE, and TA/8-HQ@LDH-DE. The crystal structures of the samples were characterized by X-ray diffraction (XRD, Shimadzu XRD-7000, Cu K α radiation, $2\theta = 5\text{--}80^\circ$, scanning rate of $5^\circ/\text{min}$). X-ray photoelectron spectroscopy (XPS) was used to investigate the surface elemental composition and chemical states of the samples. The surface morphology, internal structure, and evolution of the microstructure were observed by field-emission scanning electron microscopy (FE-SEM), combined with energy-dispersive X-ray spectroscopy (EDS) for elemental mapping and distribution analysis. Thermogravimetric analysis (TGA, LS00-HS-TGA-

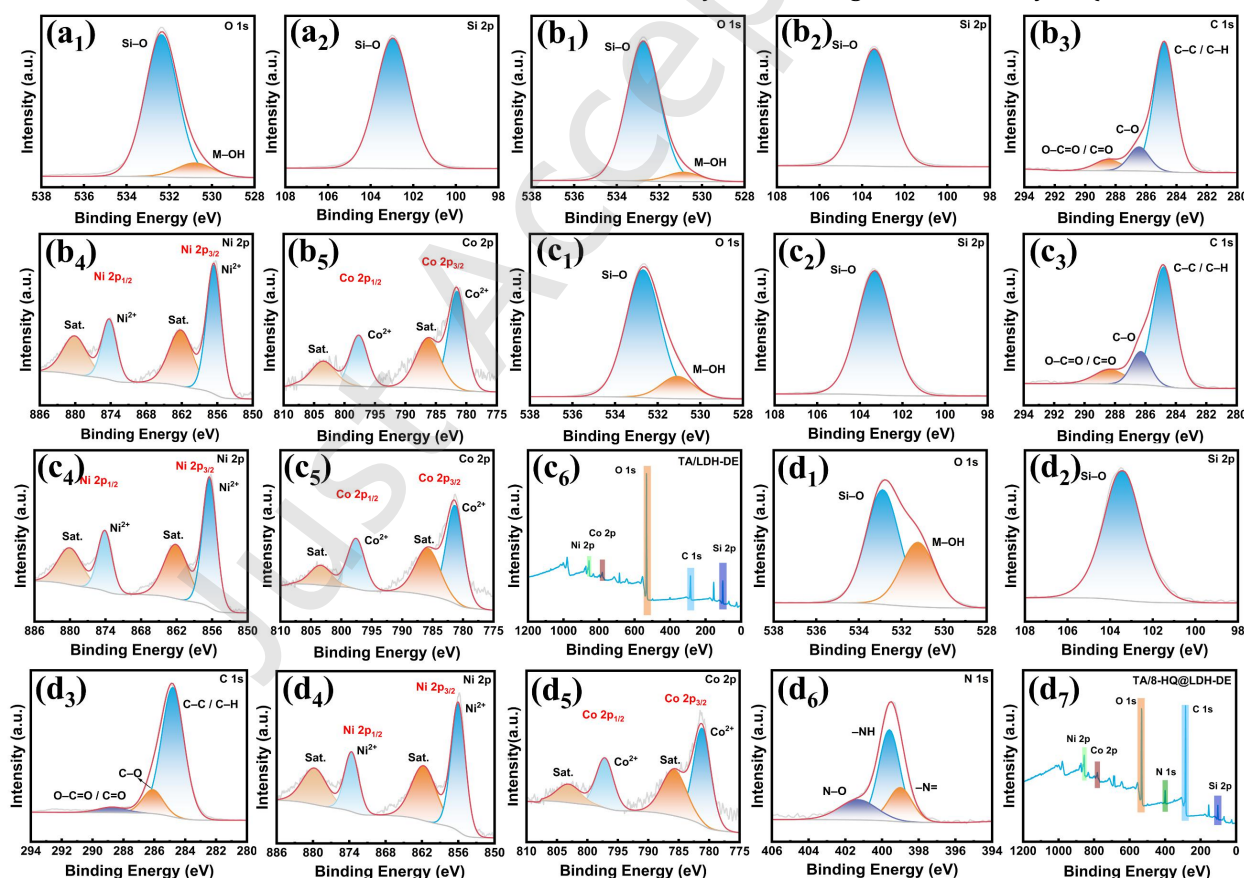


Fig. 3 XPS spectra of : (a) DE, (b) LDH-DE (c) TA/LDH-DE, (d) TA/8-HQ@LDH-DE, full survey spectrum: (c₆) TA/@LDH-DE and (d₇) TA/8-HQ@LDH-DE.

field. Both van der Waals interactions and long-range electrostatic interactions were considered during the simulations, with the electrostatic cutoff distance set to 10 Å. To ensure that all systems reached a stable thermodynamic

101, under N₂ atmosphere, heating rate of 10°C/min) was carried out to evaluate the thermal stability of the composite corrosion inhibitor and determine the loading content of 8-HQ.

3 Results and discussion

3.1 Analysis of the surface morphology and chemical structure of fillers

The micromorphology of DE upon stepwise surface modification was characterized by SEM and EDS (Fig. 2(a-j)). Pristine DE exhibits a hollow shell morphology of 30–40 μm with a porous surface, providing abundant active sites for corrosion inhibitor loading. After in-situ hydrothermal growth of LDH (Fig. 2(b)), the DE surface is uniformly covered by flaky nanocrystals, indicating successful LDH growth and successful functionalization of the support. Following TA modification (Fig. 2(c₁–c₃)), a wrinkled organic thin film forms on the sample surface, while the layered LDH structure remains intact without obvious damage. After loading 8-HQ (Fig. 2(d₁–d₃)), the morphology is highly similar to that of TA/LDH-DE, with no structural collapse or agglomeration, confirming the successful introduction of 8-HQ without damaging the support structure, which is favorable for the stable loading and controlled release of the corrosion inhibitor. The EDS results show uniform distribution of cobalt and nickel, along with a characteristic nitrogen signal, confirming the successful growth of LDH and effective loading of 8-HQ.

As shown in Fig. 2(k), Fourier-transform infrared spectroscopy (FTIR) was used to characterize DE, 8-HQ, LDH-DE, TA/LDH-DE, and TA/8-HQ@LDH-DE. DE showed Si-O-Si (1095 cm^{-1}) and Si-OH (793 cm^{-1}) peaks (SiO_2 framework). 8-HQ exhibited aromatic C-H (3044 cm^{-1}) and quinoline ring C=C/N (1580 cm^{-1}) peaks. LDH-DE displayed -OH (3460 cm^{-1}), O-H bending (1640 cm^{-1}), and NO_3^- N-O (1395 cm^{-1}) peaks, confirming LDH loading. TA/LDH-DE had a TA-derived C=O peak (1714 cm^{-1}), indicating successful TA grafting. TA/8-HQ@LDH-DE showed all characteristic peaks of the above components,

As presented in Fig. 2(l), XRD results demonstrate the successful in-situ growth of LDH on DE. The sample exhibits characteristic diffraction peaks of both SiO_2 and LDH. After TA modification and 8-HQ loading, the diffraction peak intensity of LDH decreases and the peaks become broadened, while the layered framework structure remains intact. Moreover, upon 8-HQ loading, the diffraction peaks of the composite filler are further reduced, and no obvious crystalline peaks of free 8-HQ are observed, indicating that 8-HQ exists in an amorphous or highly dispersed state. Collectively, these results confirm the successful construction of the TA/8-HQ@LDH-DE composite filler.

BET analysis further reveals the evolution of pore structure during the stepwise modification process, as presented in Fig. 2(m). Pure DE exhibits a specific surface area of $0.9804\text{ m}^2/\text{g}$, indicating limited accessible pore structure despite its inherent porous framework [40–43]. After in-situ growth of LDH, the specific surface area of LDH-DE increases significantly to $8.7674\text{ m}^2/\text{g}$ with a reduced average pore diameter, suggesting that LDH nanosheets introduce abundant interlayer gaps and pore channels. Following TA modification, TA/LDH-DE retains a relatively high specific surface area of $8.0713\text{ m}^2/\text{g}$, while its pore volume and average pore diameter decrease to $0.007472\text{ cm}^3/\text{g}$ and 5.3024 nm , respectively, implying that TA mainly occupies partial pore space without significantly destroying the framework structure. Upon further loading of 8-HQ, the specific surface area, pore volume and average pore diameter of TA/8-HQ@LDH-DE further decline to $2.5836\text{ m}^2/\text{g}$, $0.001250\text{ cm}^3/\text{g}$ and 1.9353 nm , respectively, demonstrating that 8-HQ fills the remaining pore channels. The N_2 adsorption-desorption data of DE, LDH-DE, TA/LDH-DE and TA/8-HQ@LDH-DE are listed in Table S1. Overall, the systematic changes in BET parameters confirm the

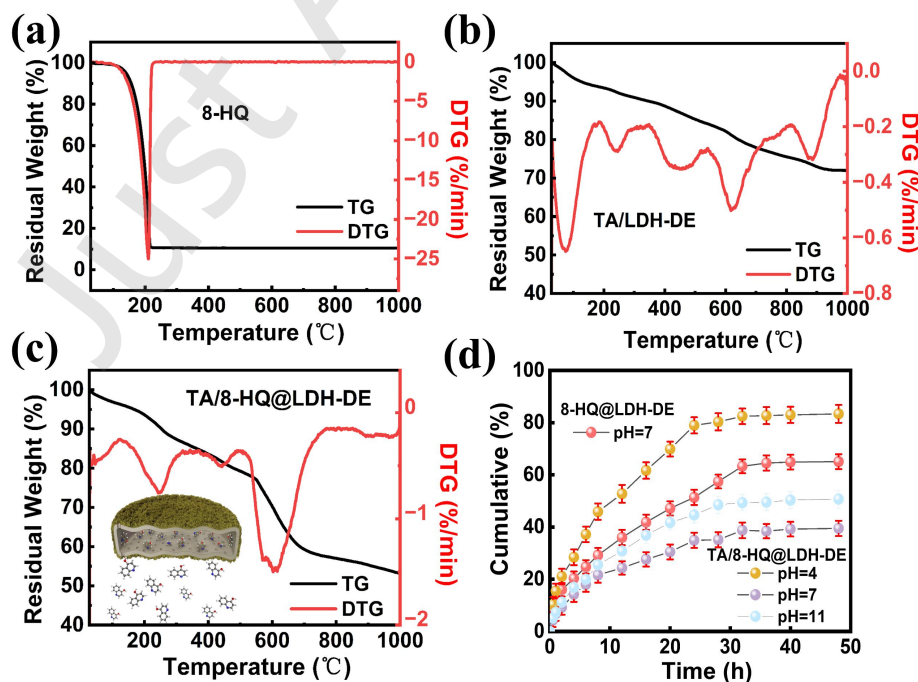


Fig. 4 TG and DTG curves of (a) 8-HQ, (b) TA/LDH-DE, (c) TA/8-HQ@LDH-DE, (d) pH-dependent release properties of TA/8-HQ@LDH-DE microcapsules.

verifying successful construction of the composite filler.

successful stepwise assembly of LDH, TA and 8-HQ. The

schematic diagram of the synthesis of TA/8-HQ@LDH-DE material is shown in Fig. 2(n).

To further analyze the chemical structure of the as-prepared filler, X-ray photoelectron spectroscopy (XPS) was performed, as shown in Fig. 3. Pure DE exhibited characteristic Si-O peaks of Si 2p and O 1s, providing a stable substrate for subsequent modification. After loading NiCo-LDH, the M-OH peak in O 1s was significantly enhanced, accompanied by the appearance of Ni 2p, Co 2p and their corresponding satellite peaks, confirming the successful in-situ growth of NiCo-LDH on the DE surface with stable Ni^{2+} and $\text{Co}^{2+}/\text{Co}^{3+}$ valence states. After modification with TA, the peak areas of C-O and O-C=O in C 1s increased remarkably, indicating that TA was grafted onto LDH via coordination through phenolic hydroxyl groups. Upon final loading of 8-HQ, a characteristic N 1s peak emerged for the first time, directly verifying the successful immobilization of 8-HQ. The Si 2p peak shape remained stable throughout the process, and the gradual shift in the binding energies of Ni/Co 2p further validated the coordination interaction between organic components and LDH. In summary, the XPS results fully confirm the successful synthesis of the TA/8-HQ@NiCo-LDH-DE composite filler.

3.2 Analysis of the chemical structure and thermal stability of filler

Thermogravimetric analysis (TGA) of the composite filler was carried out from 25 to 1000 °C to evaluate its thermal stability and estimate the loading content of 8-HQ, as presented in Fig. 4. DE exhibits high thermal stability; thus,

the mass loss of the samples mainly arises from the removal of adsorbed/interlayer water and the decomposition of organic components [44, 45]. Pure 8-HQ starts to decompose at approximately 115°C, with the main decomposition completed at around 220°C, indicating low thermal stability. TA/LDH-DE shows multistage weight loss with a char residue of 29.33% at 1000°C, primarily attributed to water removal, dehydroxylation of LDH layers, and decomposition of TA. Similarly, TA/8-HQ@LDH-DE displays multistage weight loss but exhibits an additional weight loss within the decomposition temperature range of 8-HQ, confirming the successful loading of 8-HQ. Its char residue at 1000°C increases to 54.93 wt.%, which is significantly higher than that of TA/LDH-DE. This elevated thermal residue suggests enhanced organic-inorganic interfacial interactions and increased carbonaceous residues, further verifying the successful construction of the composite filler. Based on the characteristic weight-loss behaviors of 8-HQ and TA/LDH-DE, together with the overall thermogravimetric profile of the TA/8-HQ@LDH-DE composite filler, the loading content of 8-HQ was calculated using Equations (1) and (2). Herein, $M_{\text{TA/LDH-DE}}$ and $M_{8\text{-HQ}}$ represent the mass fractions of TA/LDH-DE and 8-HQ, respectively. According to the mass-loss difference method, the loading amount of 8-HQ was determined to be 25.97 wt.%, while the remaining 74.03 wt.% was attributed to the TA/LDH-DE framework. The corresponding calculation results and detailed data are summarized in Table S2. Thus, the TGA results confirm from both thermal behavior and quantitative analysis that 8-HQ has been successfully loaded

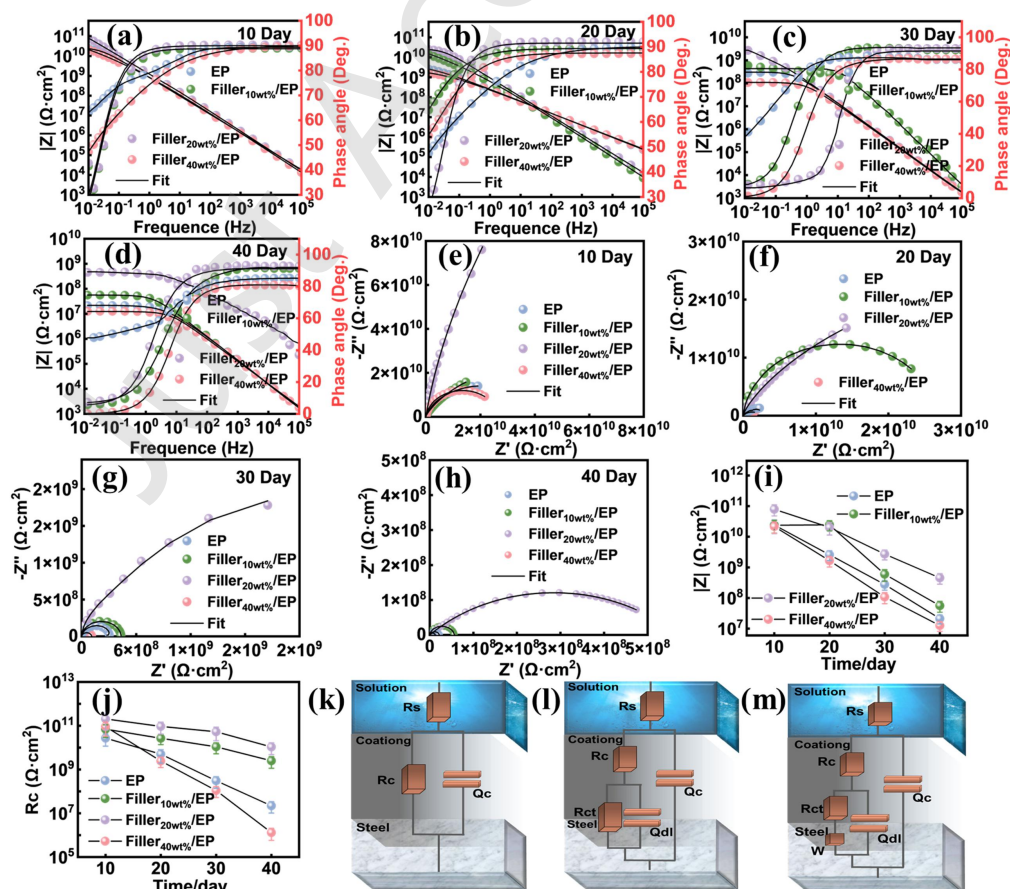


Fig. 5 Bode, Phase Angle and Nyquist diagrams of EP, 10 wt.%, 20 wt.% and 40 wt.% Filler/EP coatings immersed in 3.5 wt.% NaCl solution with different time: (a) and (e) 10 days, (b) and (f) 20 days, (c) and (g) 30 days, (d) and (h) 40 days, (i) $|Z|_{f=0.01 \text{ Hz}}$, (j) The value of R_c , (k) $R(\text{QR})$ fitting circuit, (l) $R(\text{Q(RQR)})$ fitting circuit, (m) $R(\text{Q(RQ(RW))))$ fitting circuit.

into the TA/LDH-DE carrier.

$$89.95\% \times M_{TA/LDH-DE} + 29.33\% \times M_{8-HQ} = 45.07\% \quad (1)$$

$$M_{TA/LDH-DE} + M_{8-HQ} = 100\% \quad (2)$$

As shown in Fig. 4(d), the slower release of 8-HQ after TA modification can be attributed to the formation of stronger chemical interactions between TA and the LDH-DE matrix. TA, with its polyphenolic structure, can create strong hydrogen bonds and coordinate with metal ions in the LDH, enhancing the stability of the structure. These chemical bonds between TA and the LDH-DE matrix effectively trap 8-HQ within the system, slowing its release. In contrast, without TA, 8-HQ is more weakly adsorbed, leading to a faster release. Meanwhile, 8-HQ exhibits pH-responsive sustained release behavior. As shown in Fig. 4 (d), both 8-HQ@LDH-DE and TA/8-HQ@LDH-DE exhibit a typical two-stage release behavior, consisting of an initial rapid release stage followed by a gradual sustained-release stage. For TA/8-HQ@LDH-DE, the release amount strongly depends on the surrounding pH environment. Under acidic conditions (pH = 4), the Ni-Co LDH layers are partially dissolved due to the attack of H⁺ ions, resulting in the destruction of the LDH-based nanocontainer structure and the fastest release of 8-HQ. Under alkaline conditions (pH = 11), the increased OH⁻

concentration influences the interlayer anion exchange equilibrium of LDH, thereby promoting the diffusion and release of partially loaded 8-HQ molecules. In contrast, under neutral conditions (pH = 7), the relatively stable LDH layered structure and strong interaction between the loaded inhibitor and carrier effectively retard inhibitor diffusion, leading to a sustained-release behavior. Therefore, the different release profiles under various pH environments confirm the pH-responsive sustained release capability of the TA/8-HQ@LDH-DE filler.

3.3 Analysis of the Electrochemical Properties of Composite Coatings

Electrochemical Impedance Spectroscopy (EIS) was employed to characterize various coating systems, as shown in Fig. 5, with the low-frequency impedance modulus $|Z|_{0.01\text{Hz}}$, capacitive arc radius in Nyquist plots, and coating resistance R_c derived from equivalent circuit fitting used as key indicators for corrosion resistance [46-48]. Among these parameters, R_c serves as a key indicator for characterizing coating compactness and resistance to corrosive medium penetration—a higher R_c value signifies a denser coating structure and stronger anti-penetration performance. Long-term immersion tests were carried out in 3.5 wt.% NaCl solution at 25°C for 40 days. The variation in coating

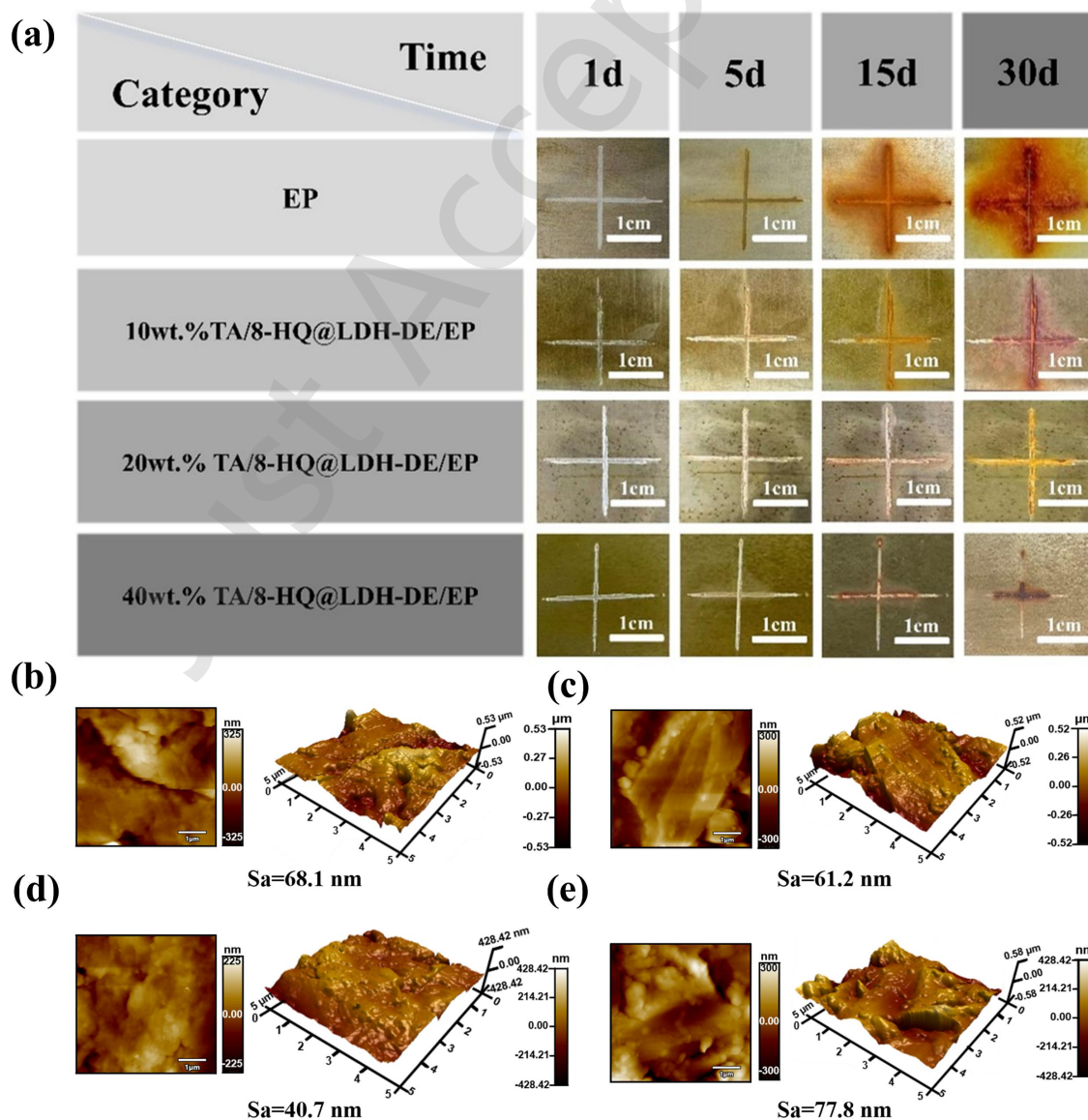


Fig. 6 (a) Macroscopic images of epoxy scratch coatings with different microcapsule contents (0, 10, 20, 40 wt.%) after immersion in 3.5 wt.% NaCl solution (1, 5, 15, 30 days). AFM images of coatings with different microcapsule contents after 5 days of salt spray test (b) 0 wt.%, (c) 10 wt.%, (d) 20 wt.% and (e) 40 wt.%

resistance R_c was obtained by fitting Nyquist plots at different immersion stages using ZSimpWin software (shown in Table S3). During immersion, the R_c values of all coatings decreased gradually as corrosive media penetrated the coating interior.

After 40 days of immersion, the R_c of the neat EP coating dropped to $2.21 \times 10^7 \Omega \cdot \text{cm}^2$, indicating a significant degradation in its protective performance. In contrast, the 20 wt.% Filler/EP composite coating maintained a remarkably high R_c value of $1.07 \times 10^{10} \Omega \cdot \text{cm}^2$, nearly three orders of magnitude higher than that of the neat EP coating, demonstrating the most excellent long-term corrosion protection. Supporting evidence confirmed that the $|Z|_{0.01\text{Hz}}$ value of the Filler_{20wt.%}/EP coating reached $4.52 \times 10^8 \Omega \cdot \text{cm}^2$, far exceeding those of the pure EP coating ($2.11 \times 10^7 \Omega \cdot \text{cm}^2$), Filler_{10wt.%}/EP coating ($5.59 \times 10^7 \Omega \cdot \text{cm}^2$), and Filler_{40wt.%}/EP coating ($1.25 \times 10^7 \Omega \cdot \text{cm}^2$). It also exhibited the largest capacitive arc radius in Nyquist plots, consistent with the R_c results. These findings verify that 20 wt.% is the optimal filler loading for this coating system, where synergistic effects between the filler and epoxy matrix enable balanced physical barrier protection and active corrosion inhibition.

3.4. Analysis of salt spray test and surface roughness of coatings

Four epoxy composite coatings with 0, 10, 20, and 40 wt.% TA/8-HQ@LDH-DE microcapsules were prepared on Q235 steel substrates to evaluate their corrosion protection. The coatings were immersed in 3.5 wt.% NaCl solution at room temperature for 30 days. As shown in Fig. 6(a), the macroscopic corrosion of scratched coatings was recorded at

wt.% TA/8-HQ@NiCo-LDH-DE/EP coating showed the best corrosion resistance, with only slight rust confined to the scratch. This is attributed to the synergistic barrier, ion adsorption, and rust conversion effects of the filler. These results confirm that 20 wt.% is the optimal loading for high-performance anti-corrosion coatings. To evaluate its practical engineering potential, the anti-corrosion performance of the 20 wt.% composite coating was compared with reported commercial rust converters and marine epoxies (Table S4). After 40 days of immersion, our coating still maintains an ultrahigh coating resistance of 1.07×10^{10} and achieves a 30-day neutral salt spray resistance, which is significantly superior to most reference coatings.

The effect of TA/8-HQ@LDH/DE filler content on the micromorphology and surface roughness of coatings was investigated via atomic force microscopy (AFM). The incorporation of microcapsule fillers into epoxy coatings significantly influences the surface topography and roughness parameters, as nanoparticle addition generally increases surface roughness while improving mechanical properties [52-54]. AFM characterization was performed on scratched steel substrates covered with filler-free coatings and coatings containing 10 wt.%, 20 wt.%, and 40 wt.% TA/8-HQ@LDH/DE fillers, and the results are presented in Fig. 6(b-e). The filler-free coating exhibited an arithmetic mean surface roughness (S_a) of 68.1 nm. A significant increase in surface roughness was observed after 5 days of salt spray testing, which was attributed to the accumulation of corrosion products and indicated severe corrosion of the metal substrate. With the filler content increasing from 10

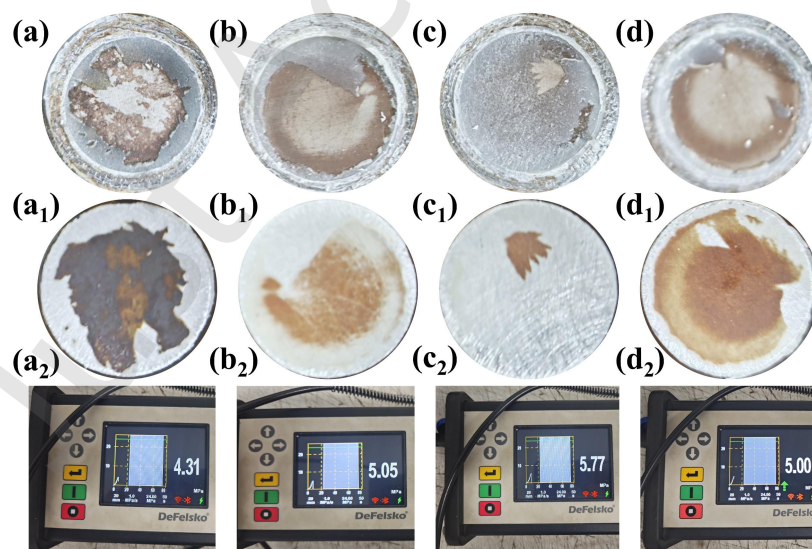


Fig. 7 Pull-off adhesion test results and fracture morphology comparison of pure coating and different content of TA/8-HQ@LDH-DE composite coating: (a) pure coating, (b-d) composite coatings containing 10 wt.%, 20 wt.% and 40 wt.% TA/8-HQ@LDH-DE filler.

different immersion times [49-51]. The results reveal that corrosion at the scratch differs significantly with increasing immersion time. The neat EP coating showed severe corrosion with extensive rust propagation after 30 days. The 10 wt.% filler coating provided limited long-term protection, while the 40 wt.% coating exhibited reduced performance due to excessive filler-induced defects. In contrast, the 20

wt.% ($S_a = 61.2 \text{ nm}$, Fig 6(c)) to 20 wt.% ($S_a = 40.7 \text{ nm}$, Fig 6(d)), the coating surface roughness decreased gradually, and the surface particles became more uniformly and densely distributed. This demonstrates that moderate fillers can disperse uniformly in the coating matrix and fill microscopic defects effectively, forming a smoother and denser coating structure. However, when the filler content

further increased to 40 wt.% (Fig 6(e)), the surface roughness rose sharply to 77.8 nm. Remarkable particle agglomeration and surface protrusions were observed in AFM images. Excessive fillers reduced the dispersion uniformity in the matrix and caused particle agglomeration, resulting in prominent surface undulations and structural defects. These results confirm that the optimal dispersion state of TA/8-HQ@LDH/DE fillers is obtained at a content of 20 wt.%. The corresponding coating possesses the densest and smoothest surface structure, endowing the metal substrate with excellent anticorrosion performance.

3.5. Adhesion test

Fig. 7 systematically presents the peel adhesion strength and corresponding fracture morphologies of pristine EP coating and composite coatings filled with 10 wt.%, 20wt.% and 40wt.% TA/8-HQ@LDH-DE fillers. The adhesion strength of the pure EP coating is 4.31 MPa. After introducing 10%, 20% and 40% fillers, the adhesion strength rises to 5.05 MPa, 5.77 MPa and 5.0 MPa respectively. Such strength enhancement is mainly related to the interface regulation effect derived from complexes formed by the reaction between tannic acid and rust on the substrate surface. It is obviously observed that the coating with 20% filler achieves the optimal adhesion performance. Specifically, the tannic acid content is insufficient at 10% filler loading and fails to exert sufficient interfacial modification effect, while

and maximize coating adhesion, while overloading induces filler agglomeration and weakens the modification effect of tannic acid, thereby causing performance decline. This conclusion provides reliable guidance for the optimized proportion design of fillers in composite anticorrosive coatings.

3.6. The establishment of simulation model and mechanism analysis

In this study, molecular dynamics simulations were performed to investigate the diffusion behavior of corrosive media in four coatings: pure EP, LDH-DE/EP, TA/LDH-DE/EP, and TA/8-HQ@LDH-DE/EP [55-57]. Although existing diffusion models have certain limitations, they provide theoretical support for the qualitative comparison of coating barrier properties. Based on Einstein's diffusion theory, the diffusion coefficient D was adopted as a key indicator and obtained by fitting the mean squared displacement (MSD) curves [58]. The MSD and D were calculated according to Equation 3 and Equation 4, respectively. The result show that the diffusion coefficient is negatively correlated with the coating barrier performance: a lower D value corresponds to stronger suppression of corrosive medium diffusion, leading to superior barrier and corrosion resistance. The evolution of MSD curves reveals the migration of corrosive particles, offering a theoretical

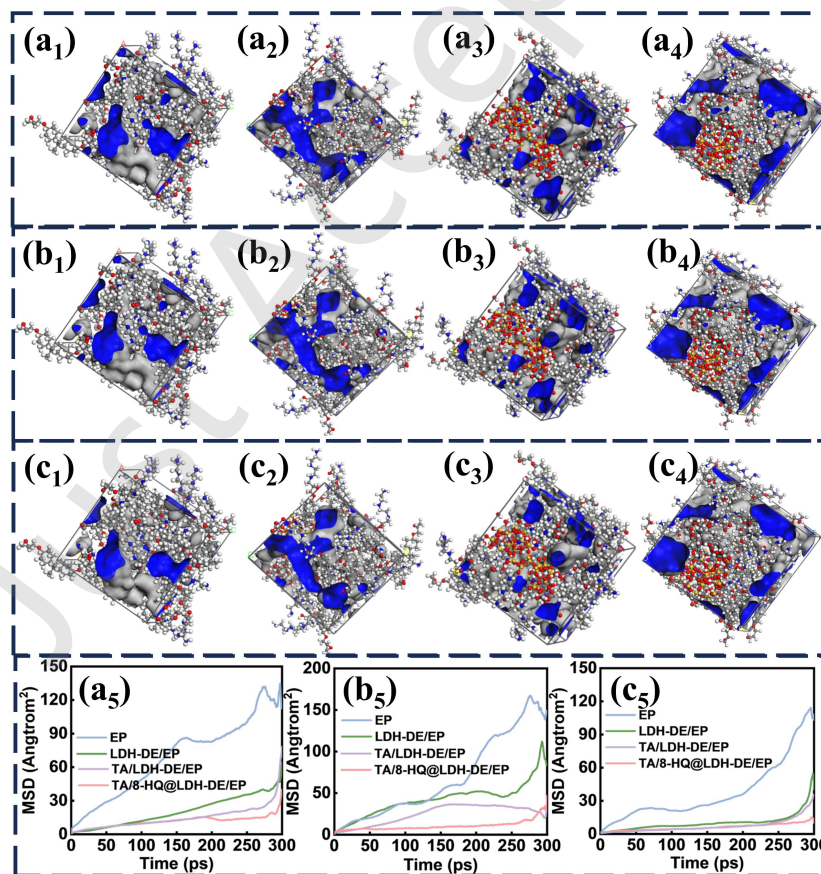


Fig. 8 Free volume distribution of EP, LDH-DE/EP, TA/LDH-DE/EP and 8-HQ@LDH-DE/EP coatings was detected using (a₁-a₄) H₂O, (b₁-b₄) O₂ and (c₁-c₄) Cl⁻, MSD curves of (a₅) H₂O, (b₅) O₂ and (c₅) Cl⁻ in the above coatings.

excessive addition of 40% fillers leads to secondary agglomeration, which damages the structural continuity of the coating and forms heterogeneous stress concentration sites at the interface. Appropriate filler addition enables tannic acid to fully exert its interfacial regulation capacity

basis for clarifying the protective mechanism of composite coatings.

$$MSD = |r_i(t) - r_i(0)|^2 \#(3)$$

Furthermore, D can be calculated by using the following

Equation:

$$D = \frac{1}{6Na} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{Na} [|r_i(t) - r_i(0)|] \quad \text{#####(4)}$$

MSD was used as a key parameter to characterize molecular diffusion. Combined with the simulation results in Fig. 8(a-c) and based on Einstein's diffusion theory, the diffusion coefficients of H₂O, O₂, and Cl⁻ in various coatings were calculated by fitting MSD curves, with the data listed in Table S5. A lower diffusion coefficient indicates a stronger barrier effect of the coating. The results show that the in the TA/8-HQ@LDH-DE/EP composite coating, which can effectively inhibit their penetration and transport, thus endowing the coating with excellent corrosion resistance.

As the free volume fraction (FFV) increases, the diffusion rate of corrosive media also increases. FFV can be defined by the following equation:

$$FFV = \frac{V_{free}}{V_{free} + V_{occupy}} \quad \text{#(5)}$$

The total volume of a polymer coating consists of atomic occupied volume and free volume. Free volume is formed by the random packing of polymer chains and provides pathways for the diffusion of corrosive media. In this study, the coating microstructure was quantitatively characterized using occupied volume and free volume, and the FFV was calculated accordingly. A higher FFV facilitates easier penetration and migration of corrosive species. Using H₂O, O₂, and Cl⁻ as probes, the free volume distribution in

The results demonstrate that the TA/8-HQ@LDH-DE/EP composite coating exhibits a lower FFV, which effectively inhibits the penetration of corrosive media toward the metal substrate, leading to superior barrier and corrosion resistance properties. This conclusion is consistent with the EIS test results.

Fig. 9(a-b) shows the molecular electrostatic potential (MEP) distributions of the DFT-optimized TA-Fe²⁺ and 8-HQ-Fe²⁺ complexes [59, 60]. The low-potential regions of TA and 8-HQ are mainly concentrated around oxygen-containing functional groups and adjacent coordination moieties. These regions are highly electronegative and electron-donating, acting as preferential coordination sites for Fe²⁺. Binding energy calculations confirm strong interactions between both ligands and Fe²⁺, leading to the formation of stable complexes.

$$E_{ad} = E_{ab} - E_{TA} - E_{Fe} \quad \text{##(6)}$$

$$E_{ad} = E_{ab} - E_{8-HQ} - E_{Fe} \quad \text{##(7)}$$

In this study, E_{ab} represents the total energy of the adsorption (or complexation) system, while E_{TA}, E_{8-HQ}, and E_{Fe} correspond to the energies of the isolated TA molecule, 8-HQ molecule, and Fe²⁺, respectively. The binding energies (E_{ad}) of TA-Fe²⁺ and 8-HQ-Fe²⁺ were calculated via Equation 3 and Equation 4, with the results summarized in Table S7. Their values are negative (-2.9218 eV and -1.9053 eV, respectively), indicating that the coordination between

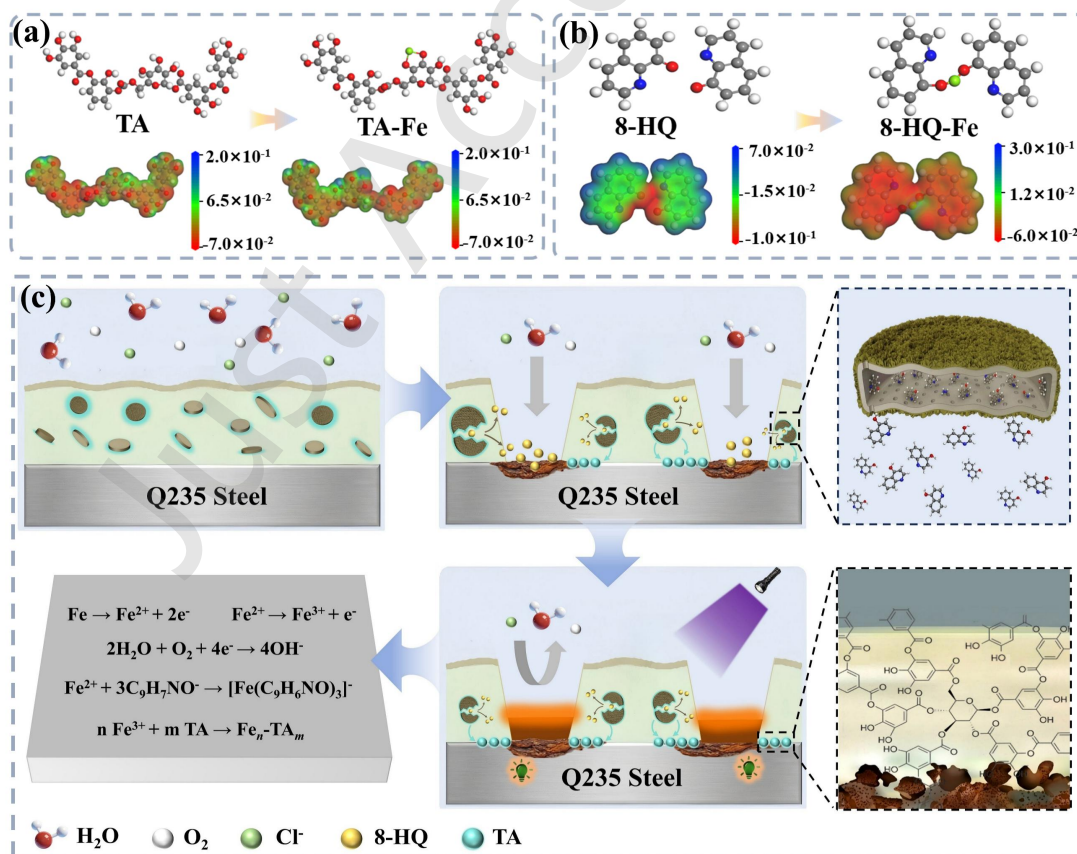


Fig. 9 (a-b) DFT process of the complexation of TA/8-HQ and Fe²⁺, (c) Schematic diagram of anti-corrosion mechanism of TA/8-HQ@LDH-DE/EP composite coating.

different coatings is shown in Fig. 8(a-c), with FFV data listed in Table S6.

TA or 8-HQ and Fe²⁺ is thermodynamically spontaneous and yields highly stable complexes. This also reflects strong

coordination interactions between TA or 8-HQ and Fe^{2+} .

The excellent corrosion resistance of the TA/8-HQ@DE-LDH/EP composite coating originates from the synergistic effects of hierarchical structural shielding, controlled release of loaded corrosion inhibitors, rust layer conversion, and enhanced interfacial stability. As shown in Fig. 9(c), LDH grows in-situ on the DE framework to form a hierarchical porous structure, which prolongs the diffusion pathways of corrosive species (H_2O , O_2 , Cl^-) and strengthens the physical barrier performance of the coating.

The porous LDH-DE carrier provides sufficient loading sites for 8-HQ, enabling sustained release of the corrosion inhibitor and its functionalization at the metal/coating interface. The polyphenolic hydroxyl groups of TA coordinate with Fe^{2+} in the rust layer, promoting the conversion of the rust layer into a stable protective layer and the formation of a passive film, thereby improving the adhesion between the coating and the rusted substrate as well as the long-term stability of the system.

4 Conclusion

TA/8-HQ@DE-LDH/EP composite coating was successfully fabricated in this work for the long-term corrosion protection of pre-rusted Q235 carbon steel. LDH was grown on DE to form a hierarchical porous structure, achieving an 8-HQ loading capacity of approximately 25.97%. Electrochemical measurements reveal that the coating with 20 wt.% filler exhibits the highest impedance and optimal protective performance after 40 days of immersion in 3.5 wt.% NaCl solution. Molecular dynamics simulations confirm that it effectively hinders the diffusion of corrosive species and promotes the formation of a compact and stable interfacial layer. Benefiting from the synergistic effects of a hierarchical barrier effect, controlled release of corrosion inhibitors, and interfacial stabilization, the coating provides efficient and long-lasting protection for rusted steel substrates, demonstrating promising application prospects in the in-situ repair and long-life corrosion protection of steel structures.

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Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in

this work.

Author contribution statement

F. G.: Investigation, visualization, writing-original draft, writing-review & analysis. J. Y. C.: Investigation, visualization, writing-original draft, writing-review & analysis. X. Y. L.: Investigation. Y. X. Z.: Project administration, funding acquisition, investigation, visualization, writing-original draft, writing-review & editing, formal analysis. All the authors have approved the final manuscript

Ethics statement

"Not applicable" could be provided for biological studies with no human or animals involved.

Use of AI statement

None.

References

- [1] Kassinis, C.; Aresti, L.; Koronides, M.; Christodoulides, P.; Michailides, C.; Onoufriou, T. A review on the environment's influence on coastal marine steel corrosion and in-situ monitoring. *J. Mater. Sci.: Mater. Eng.* **2025**, *20*, 125.
- [2] Napte, K.; E. Kondhalkar, G.; Vishal Patil, S.; Vishnu Kharat, P.; Snehal Mayur, B.; Sidhappa Kurhade, A.; Shital Yashwant, W. Recent advances in sustainable concrete and steel alternatives for marine infrastructure. *Sustain. Mar. Struct.* **2025**, *7*, 107-131.
- [3] Bajić, P.; Leporace-Guimil, B.; Andrade, C.; Tošić, N.; de la Fuente, A. Chloride-induced corrosion effects on the structural performance of concrete with rebar and fibres: a review. *Appl. Sci.* **2025**, *15*, 6457.
- [4] Liu, L.; Li, W.; Deng, Z.; Xu, S.; Xu, Y.; Zeng, L.; Li, D.; Yang, Y.; Zhong, Z. Effect of moisture on corrosion behavior of Q235 steel in bentonite clay. *Int. J. Electrochem. Sci.* **2023**, *18*.
- [5] Liu, G.; Gong, Z.; Yang, Y.; Shi, J.; Liu, Y.; Dou, X.; Li, C. Electrochemical dissolution behavior of stainless steels with different metallographic phases and its effects on micro electrochemical machining performance. *Electrochem. Commun.* **2024**, *160*, 107677.
- [6] Loto, R. T.; Oladipupo, S.; Folarin, T.; Okosun, E. Impact of chloride concentrations on the electrochemical performance and corrosion resistance of austenitic and ferritic stainless steels in acidic chloride media. *Discover Applied Sciences* **2025**, *7*, 672.
- [7] Guo, F.; Yin, H.; Liu, H.; Ma, J.; Luo, H.; Li, H. Hollow ZIF-8 microcapsules loaded with tannic acid for smart self-healing anticorrosion coatings. *Surf. Sci. Technol.* **2026**, *4*, 16.
- [8] Liu, S.; Guo, F.; Song, H.; Yin, Y.; Kang, S.; Wu, C.; Zhang, Y. Sustained-release diatomite microcapsules are used in hydrophobic coatings to achieve multiple synergistic anti-corrosion. *Chem. Eng. J.* **2025**, *526*, 170608.
- [9] Liu, S.; Zhang, X.; Rao, J.; Yu, L.; Lu, W.; Zhou, H.; Chen, S.; Zhang, Y.; Liu, X. Ni-Co hydrotalcite modified diatom to achieve corrosion inhibition and Cl^- adsorption for long-term corrosion protection of steel. *Corros. Sci.* **2023**, *225*, 111589.
- [10] Lu, W.; Zhang, X.; Yin, C.; Zhao, W.; Liu, S.; Rao, J.; Zhang, Y. X.; Liu, X. Diatomite@ MoS_2 nanocomposite layers as composite coating targeting for Mg alloys endowed with properties of anticorrosion and antiwear. *Langmuir* **2024**, *40*, 8233-8247.
- [11] Guo, X.; Zhu, J.; Kang, J.; Duan, M.; Wang, Y. Rust layer adhesion capability and corrosion behavior of weathering steel under tension during initial stages of simulated marine atmospheric corrosion. *Constr. Build. Mater.* **2020**, *234*, 117393.

- [12] Li, Y.;Lei, B.; Guo, X. Influence of phosphoric acid on the adhesion strength between rusted steel and epoxy coating. *Coatings* **2021**, *11*, 246.
- [13] Li, W.;Fan, Z.;Li, X.;Jiang, B.;Yan, F.;Zhang, Z.; Wang, X. Improved anti-corrosion performance of epoxy zinc rich coating on rusted steel surface with aluminum triphosphate as rust converter. *Prog. Org. Coat.* **2019**, *135*, 483-489.
- [14] Ren, K.;Zhang, J.;Liu, Y.;Hou, Q.;Zhang, R.;Krishnamurthy, M.;Zuo, Z.;Zhao, Y.; Yu, Z. Failure mechanisms and corrosion behavior of epoxy-based protective coatings prepared on 20# steel exposed to cooling water. *Int. J. Electrochem. Sci.* **2025**, *20*, 101207.
- [15] Tian, Q.;Huang, S.;Tang, D.;Li, H.;Zhang, Y.;Huang, Z.;Hu, H.; Gan, T. High-solid and water-based epoxy resin anti-corrosion coatings for complex construction environments: Synergistic effect of inorganic-organic hybrid and grafted long chain structure. *Appl. Surf. Sci.* **2025**, *687*, 162299.
- [16] Chen, T.;Tian, Y.;Guo, Z.;Chen, Y.;Qi, Q.; Meng, F. Design of novel RGO/2D strip-like ZIF-8/DMAOP ternary hybrid structure towards high-efficiency microwave absorption, active and passive anti-corrosion, and synergistic antibacterial performance. *Nano Res.* **2023**, *17*, 913-926.
- [17] Son, G.-C.;Hwang, D.-K.;Jang, J.;Chee, S.-S.;Cho, K.;Myoung, J.-M.; Ham, M.-H. Solution-processed highly adhesive graphene coatings for corrosion inhibition of metals. *Nano Res.* **2018**, *12*, 19-23.
- [18] Yang, K.;Duan, Y.;Liu, G.;Ma, G.;Fu, H.;Chen, X.;Wang, M.;Zhu, G.;Yang, W.; Shen, Y. Smart ZnS@C filler for super-anticorrosive self-healing zinc-rich epoxy coating. *Nano Res.* **2022**, *15*, 4756-4764.
- [19] Quy, B. M.;Chinh, N. T.;Anh, N. T. K.;Tuyet, V. T.;Thai, N. X.;Trung, V. Q.;Quyen, N. T. C.;Tan, N. N.; Hoang, T. Modification of hydrotalcite loading tannic acid with organic silane and application in anticorrosive epoxy coating. *ChemistryOpen* **2024**, *13*, 202400120.
- [20] Sesia, R.;Spriano, S.;Sangermano, M.; Ferraris, S. Natural polyphenols and the corrosion protection of steel: Recent advances and future perspectives for green and promising strategies. *Metals* **2023**, *13*, 1070.
- [21] Wang, X.;Zhu, Q.;Liu, X.; Hou, B. Rust conversion performance of phosphoric acid-gallic acid in vinyl chloride acrylic emulsion. *Coatings* **2021**, *11*, 152.
- [22] Yu, P.;Lei, Y.;Luan, Z.;Zhao, Y.; Peng, H. Effect on the surface anticorrosion and corrosion protection mechanism of integrated rust conversion coating for enhanced corrosion protection. *ACS Omega* **2022**, *7*, 8995-9003.
- [23] Guo, F.;Liu, X.;Liu, S.;Song, H.;Rao, J.; Zhang, Y. Hierarchical lamellar ZIF-8-based epoxy coatings with time-adaptive, pH-triggered stepwise inhibitor release for durable corrosion protection of magnesium alloys. *Nano Res.* **2026**, *19*, 94908635.
- [24] Cao, L.;Piao, J.;Wang, W.;Fan, W.;Han, D.;Pei, Y.;Chen, Y.; Zhang, Y. Co-Al hydrotalcite assembled nanofibers to enhance corrosion inhibition and effective Cl⁻ adsorption for long-term corrosion protection. *Chem. Eng. J.* **2024**, *495*, 153052.
- [25] Mahmood, M.;Mubeen, M.;Wang, W.;Tabish, M.;Murtaza, H.;Jawad, M.;Wang, J.;Lv, Y.;Zhao, J.; Fan, B. Mechanically robust and self-healing protective coating for Zn-Al-Mg coated steel enhanced by benzotriazole-5 carboxylic acid intercalated MgAlCe ternary LDH. *Prog. Org. Coat.* **2025**, *201*, 109107.
- [26] Xu, T.;Wang, Q.-Y.;Zhang, J.-T.; Hu, J.-M. Electrodeposited graphene/layered double hydroxides micro/nanocontainers for both passive and active corrosion protection. *npj Mater. Degrad.* **2024**, *8*, 22.
- [27] Shi, S.;Ocampo-Pérez, R.;Lv, J.;Liu, Q.;Nan, F.;Liu, X.;Xie, S.; Feng, J. Diatomite cross-linked β -Cyclodextrin polymers: A novel vision of diatomite adsorbent for the removal of bisphenol A. *Environ. Technol. Innovation* **2021**, *23*, 101602.
- [28] Wang, Y.;Wang, T.;Liu, S.;Wei, Z.;Zhang, T. C.; Yuan, S. Bilayer diatomite-based composite coatings with superhydrophobic and self-healing properties for enhanced anticorrosion of AZ31B magnesium alloys. *Surf. Coat. Technol.* **2024**, *489*, 131151.
- [29] Yao, J.;Zhang, G.;Zhang, Y.;Wu, X.;Liu, C.; Rao, Z. Fabrication and thermal properties of composite phase change materials based on modified diatomite for thermal energy storage. *J. Energy Storage* **2025**, *113*, 115749.
- [30] Cao, Y.;Zheng, D.;Zhang, F.;Pan, J.; Lin, C. Layered double hydroxide (LDH) for multi-functionalized corrosion protection of metals: A review. *Journal of Materials Science & Technology* **2022**, *102*, 232-263.
- [31] Phan, M. V.;Tran, T. K. T.;Pham, Q. N.;Do, M. H.;Nguyen, T. H. N.;Nguyen, M. T.;Phan, T. T.; To, T. X. H. Controllable synthesis of layered double hydroxide nanosheets to build organic inhibitor-loaded nanocontainers for enhanced corrosion protection of carbon steel. *Nanoscale Adv* **2024**, *6*, 606-619.
- [32] Wang, Y.;Zhang, M.;Liu, Y.;Zheng, Z.;Liu, B.;Chen, M.;Guan, G.; Yan, K. Recent Advances on Transition-Metal-Based Layered Double Hydroxides Nanosheets for Electrocatalytic Energy Conversion. *Adv. Sci.* **2023**, *10*, 2207519.
- [33] Kim, N.;Lee, I.;Choi, Y.; Ryu, J. Molecular design of heterogeneous electrocatalysts using tannic acid-derived metal-phenolic networks. *Nanoscale* **2021**, *13*, 20374-20386.
- [34] Li, W.;Tao, J.;Chen, Y.;Wu, K.;Luo, J.; Liu, R. Porous microspheres with corrosion sensing and active protecting abilities towards intelligent self-reporting and anti-corrosion coating. *Prog. Org. Coat.* **2023**, *178*, 107468.
- [35] Wang, R.;Cao, L.;Wang, W.;Mao, Z.;Han, D.;Pei, Y.;Chen, Y.;Fan, W.;Li, W.; Chen, S. Construction of smart coatings containing core-shell nanofibers with self-healing and active corrosion protection. *ACS Appl. Mater. Interfaces* **2024**, *16*, 42748-42761.
- [36] Zhao, X.;Yuan, Y.;Wei, Y.;Zhang, Z.; Zhang, Y. LDH-based "smart" films for corrosion sensing and protection. *Materials* **2023**, *16*, 3483.
- [37] Moirangthem, M.;Kumar, K.;Dhanda, L.; Meena, S. K. Investigating the Multifunctional Coating Design for Metal Surfaces: Insights from Molecular Dynamics Simulations. *ACS Omega* **2025**, *10*, 48900-48911.
- [38] Cao, G.;Ruan, Y.;Liu, J.;Hu, Z.; Zhu, H. Preparation and properties study of self-healing anticorrosive coating based on MCM-41 nanocontainer and triazinyl corrosion inhibitor. *Sci Rep* **2025**, *15*, 22288.
- [39] Kotb, Y.;Serfass, C. M.;Cagnard, A.;Houston, K. R.;Khan, S. A.;Hsiao, L. C.; Velez, O. D. Molecular structure effects on the mechanisms of corrosion protection of model epoxy coatings on metals. *Mater. Chem. Front.* **2023**, *7*, 274-286.
- [40] Virtanen, T.;Rudolph, G.;Lopatina, A.;Al-Rudainy, B.;Schagerlöf, H.;Puro, L.;Kallioinen, M.; Lipnizki, F. Analysis of membrane fouling by Brunauer-Emmett-Teller nitrogen adsorption/desorption technique. *Sci. Rep.* **2020**, *10*, 3427.
- [41] Liao, Q.;Dai, N.;Zhang, C.;Zhou, Q.;Zhang, Y.; Li, H. S-Cu Doubly Doped NiFe LDH@Diatomite with Adjustable Surface Characteristics for the Efficient Removal of Tetracycline. *Langmuir* **2024**, *40*, 21499-21513.
- [42] Cao, K. L. A.;Kautsar, D. B.;Kume, K.;Cao, K. A. L.;Septiani, E. L.;Hirano, T.;Tsunogi, N.;Matsukata, M.; Ogi, T. Preparation of Hierarchical Porous Zeolite Particles with Multiscale Pore Architectures through a Template-Assisted Spray Process for Enhanced Toluene Adsorption Rate. *ACS*

Appl Mater Interfaces **2025**, *17*, 24310-24326.

[43] Kondratowicz, T.;Besnard, C.;Turner, Z.;Tan, J.-C.;Chen, C.;Turnell-Ritson, R.; O'Hare, D. Templated synthesis of multi-hierarchical layered double hydroxide microspheres. *J. Mater. Chem. A* **2025**, *13*, 29138-29146.

[44] Souza, L. H. O.;Cristoforetti, A.;Cotting, F.;Reis da Costa Campos, W.;Rossi, S.; Fedel, M. Sebacate-Intercalated CaAl-LDH Pigments for Corrosion Protection of Aluminum Alloy. *ACS Omega* **2025**, *10*, 59771-59781.

[45] Marhamati, F.;Ghaderi, M.;Haddadi, S. A.;Arjmand, M.;Olivier, M.-G.; Mahdavian, M. Nitrogen-doped carbon hollow sphere capsules for a novel hybrid inhibitor based on lanthanum cations and 8-hydroxyquinoline: Synthesis, characterization, and self-healing properties in epoxy coating. *Colloid Surf. A* **2023**, *675*, 132065.

[46] Ganash, A.;Alsayed, S.; Al-Moubaraki, A. H. Anticorrosive properties of aqueous Cichorium intybus seeds extract as a sustainable-green inhibitor for aluminum corrosion in hydrochloric acid solution: An experimental and DFT/MC/MD theoretical approach. *J. Environ. Chem. Eng.* **2023**, *11*, 110227.

[47] He, Q.;Liu, D.;Zhou, Y.;Sun, T.-Y.; Huang, L.-F. Nitride coatings for environmental barriers: the key microscopic mechanisms and momentous applications of first-principles calculations. *Surf. Sci. Technol.* **2024**, *2*, 24.

[48] Zhang, Y.;Fan, X.;Li, X.;Zhang, Z.;Zhang, Y.;Chen, Z.;Ge, S.;Wang, Y.; Zhu, M. Micro-structure design of black ceramic composite surface towards photothermal superhydrophobic anti-icing. *Chem. Eng. J.* **2024**, *498*, 155101.

[49] Guo, G.;Wang, X.;Wang, W.;Zou, F.;Tian, W.; Cao, W. Self-healing microcapsules integrating montmorillonite and hydrotalcite: A corrosion inhibition strategy in multiple polluted environments. *Nano Res.* **2025**, *18*, 94908142.

[50] Gharieh, A.;Sharifian, A.; Dadkhah, S. Enhanced long-term corrosion resistance and self-healing of epoxy coating with HQ-Zn-PA nanocomposite. *Sci Rep* **2025**, *15*, 8154.

[51] Ismail, N. A.;Shakoor, R. A.;Al-Qahtani, N.; Kahraman, R. Multilayered LDH/Microcapsule Smart Epoxy Coating for Corrosion Protection. *ACS Omega* **2023**, *8*, 30838-30849.

[52] Fredi, G.;Simon, F.;Sychev, D.;Melnyk, I.;Janke, A.;Scheffler, C.; Zimmerer, C. Bioinspired Polydopamine Coating as an Adhesion Enhancer Between Paraffin Microcapsules and an Epoxy Matrix. *ACS Omega* **2020**, *5*, 19639-19653.

[53] Barbaz-Isfahani, R.;Saber-Samandari, S.; Salehi, M. Novel electrosprayed enhanced microcapsules with different nanoparticles containing healing agents in a single multicore microcapsule. *Int. J. Biol. Macromol.* **2022**, *200*, 532-542.

[54] Hiremath, A.;Thipperudrappa, S.; Bhat, R. Surface Morphology Analysis using Atomic Force Microscopy and Statistical Method for Glass Fiber Reinforced Epoxy-Zinc Oxide Nanocomposites. *Eng. Sci.* **2022**, *18*, 308-319.

[55] Zhang, Q.;Yu, Y.;Li, J.;Yin, C.;Tian, F.;Liu, J.; Zhou, J. Synergistic Corrosion Inhibition and UV Protection via TTA-Loaded LDH Nanocontainers in Epoxy Coatings. *Coatings* **2025**, *15*, 505.

[56] Nakamura, Y.;Higuchi, Y.;Fujii, Y.; Naito, M. Evaluation of Water Diffusion Confined in Epoxies: Role of Atomic Local Mobility of Polymer Chains. *ACS Appl. Polym. Mater.* **2025**, *7*, 5865-5873.

[57] Novell Leruth, G.;Kuznetsova, A.;Tedim, J.;Gomes, J. R. B.; Galvao, T. L. P. Molecular Dynamics Model to Explore the Initial Stages of Anion Exchange involving Layered Double Hydroxide Particles. *Nanomaterials (Basel)* **2022**, *12*, 4039.

[58] Sheng, C.;Wu, G.;Sun, X.; Liu, S. Molecular Dynamics Investigation of the Thermo-Mechanical Properties of the Moisture Invaded and Cross-Linked Epoxy System. *Polymers (Basel)* **2021**, *14*, 103.

[59] Ituen, E.;Mkpenie, V.;Yuanhua, L.; Singh, A. Inhibition of erosion corrosion of pipework steel in descaling solution using 5-hydroxytryptamine-based additives: Empirical and computational studies. *J. Mol. Struct.* **2020**, *1204*, 127562.

[60] Srivastava, V.;Haque, J.;Verma, C.;Singh, P.;Lgaz, H.;Salghi, R.; Quraishi, M. A. Amino acid based imidazolium zwitterions as novel and green corrosion inhibitors for mild steel: Experimental, DFT and MD studies. *J. Mol. Liq.* **2017**, *244*, 340-352.

[61] Díaz, B.;Nóvoa, X. R.;Pérez, C.; Rodríguez-Morgado, M. Influence of graphene oxide additions on the corrosion resistance of a rust converter primer. *Coatings* **2022**, *12*, 345.

[62] Li, S.;Wei, H.;Zhao, X.;Tang, Y.; Zuo, Y. Failure behavior and life prediction of solvent-free epoxy coatings based on impedance spectroscopy. *Electrochim. Acta* **2024**, *492*, 144349.

[63] Li, Y.;Wu, C.;Xue, M.;Cai, J.;Huang, Y.; Yang, H. Preparation of sol-gel derived anticorrosive coating on Q235 carbon steel substrate with long-term corrosion prevention durability. *Materials* **2019**, *12*, 1960.

[64] Nassar, R. U.;Alamara, K.;Balachandra, A.;Soroushian, P.; Ghebrab, T. Performance evaluation of innovative self-healing corrosion protection coatings for prestressing strands. *Heliyon* **2024**, *10*, 40681.

[65] Bagherzadeh, M. R.;Mousavinejad, T.;Akbarinezhad, E.; Ahmadi, M. Highly protective performance of water-based epoxy coating loaded with self-doped polyaniline synthesized under supercritical CO₂ condition. *Prog. Org. Coat.* **2014**, *77*, 1977-1984.

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Electronic Supplementary Material

Long-lasting corrosion protection of rusted steel via TA-driven chemical modification of LDH-diatomite and adsorption of 8-hydroxyquinoline

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The conversion performance of the TA/8-HQ@LDH-DE composite filler and pure tannic acid toward Fe^{3+} and steel corrosion products was investigated. The upper part of the Fig. S1 shows that a large amount of deep blue-black flocculent precipitate forms rapidly after adding the filler to FeCl_3 solution. In this system, TA strongly complexes with Fe^{3+} , while 8-HQ synergistically chelates to enhance iron ion capture; LDH releases active components slowly via ion exchange and adsorbs corrosive Cl^- , jointly improving the conversion efficiency. Compared with the pure tannic acid system, the composite filler generates a larger amount of precipitate at a faster reaction rate, confirming the significant synergistic enhancement of 8-HQ chelation and LDH slow-release adsorption.

After coating the rusted steel surface with the composite filler suspension and tannic acid solution respectively, uniform and dense blue-black stable rust-conversion layers were formed in both cases, which effectively solidified loose corrosion products and blocked pores in the rust layer, verifying that tannic acid can react with corrosive rust species. These tests lay a foundation for the subsequent formulation and modification of rust converters.

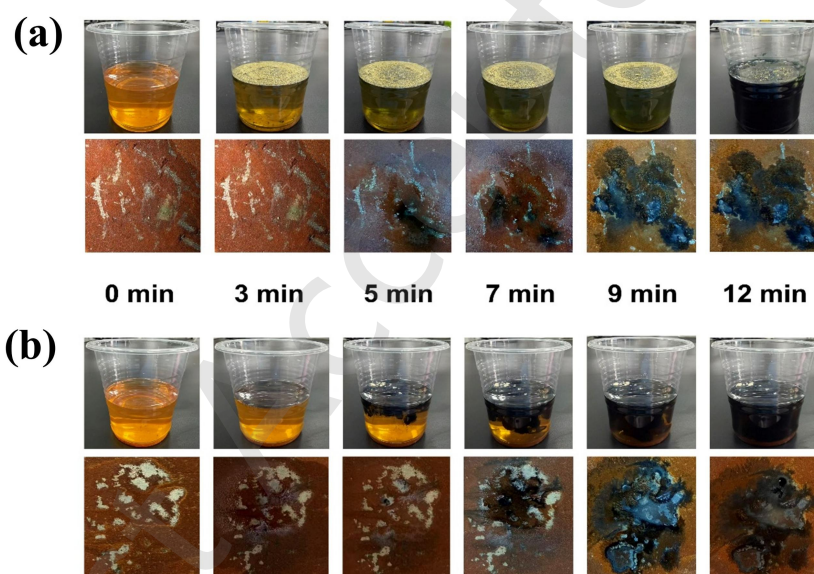


Fig. S1 Morphological changes of rusted substrates treated with (a) TA/8-HQ@LDH-DE and (b) TA.

Table S1 N_2 adsorption-desorption characterization data of DE, LDH-DE, TA/LDH-DE and TA/8-HQ@LDH-DE.

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
DE	0.9804	0.022640	15.0379
LDH-DE	8.7674	0.019971	6.1853
TA/LDH-DE	8.0713	0.007472	5.3024
TA/8-HQ@LDH-DE	2.5836	0.001250	1.9353

Table S2 Content of 8-HQ, TA/LDH-DE, and TA/8-HQ@LDH-DE in filler.

Material	Initial mass (%)	Residual mass (%)	Decomposition rate (%)	$M_{8\text{-HQ}}$ (%)	$M_{\text{TA/LDH-DE}}$ (%)
8-HQ	100	10.05	89.95		
TA/LDH-DE	100	70.67	29.33	25.97	74.03
TA/8-HQ@LDH-DE	100	54.93	45.07		

Table S3 Electrochemical parameters of each component after the sample coating were fitted.

Sample	Time	Rs ($\Omega\cdot\text{cm}^2$)	Qc	n	Rc ($\Omega\cdot\text{cm}^2$)	Qdl	n	Rct ($\Omega\cdot\text{cm}^2$)	Warbury (Y)
			$\frac{Y_0}{(\Omega^{-1}\text{cm}^{-2}\text{s}^n)}$			$\frac{Y_0}{(\Omega^{-1}\text{cm}^{-2}\text{s}^n)}$			
EP	10 d	5.67	4.31×10^{-10}	0.93	2.71×10^{10}	-	-	-	-
	20 d	11.63	6.92×10^{-10}	0.81	5.05×10^9	-	-	-	-
	30 d	13.89	1.32×10^{-10}	0.97	3.06×10^8	1.31×10^{-10}	1	1.09×10^8	-
	40 d	17.19	3.13×10^{-9}	0.71	2.21×10^7	1.18×10^{-10}	1	3.25×10^6	-
Filler _{10wt.%} /EP	10 d	7.34	2.18×10^{-10}	0.93	6.96×10^{10}	-	-	-	-
	20 d	16.62	1.87×10^{-10}	0.95	2.67×10^{10}	-	-	-	-
	30 d	27.87	6.82×10^{-9}	0.96	1.09×10^{10}	2.31×10^{-10}	0.85	5.52×10^8	-
	40 d	32.92	2.39×10^{-9}	1	2.51×10^9	1.16×10^{-9}	0.82	9.92×10^7	-
Filler _{20wt.%} /EP	10 d	26.89	1.04×10^{-10}	0.99	2.05×10^{11}	-	-	-	-
	20 d	31.03	3.78×10^{-10}	1	9.36×10^{10}	-	-	-	-
	30 d	33.52	2.31×10^{-10}	0.97	5.31×10^{10}	1.19×10^{-9}	0.78	1.25×10^9	-
	40 d	38.19	1.63×10^{-10}	0.88	1.07×10^{10}	2.43×10^{-9}	0.91	9.78×10^8	-
Filler _{40wt.%} /EP	10 d	14.98	1.19×10^{-10}	1	9.07×10^{10}	-	-	-	-
	20 d	15.88	1.38×10^{-9}	0.79	2.45×10^9	1.72×10^{-10}	0.91	2.79×10^8	-
	30 d	17.84	8.87×10^{-10}	1	1.10×10^8	9.79×10^{-10}	0.84	3.16×10^7	-
	40 d	18.31	1.52×10^{-9}	0.90	1.31×10^6	9.62×10^{-8}	0.87	1.22×10^6	1.09×10^4

Table S4 Comparison with commercial and reported anticorrosion coatings

Coating	Resin type	EIS (t)	Electrochemical value (Rc)	Salt spray	Ref.
TA/8-HQ@LDH-DE/EP	E51 bisphenol A type epoxy resin	10 d	2.05×10^{11}	30 d	This work
		20 d	9.36×10^{10}		
		30 d	5.31×10^{10}		
		40 d	1.07×10^{10}		
Oroprimer 440	Vinyl chloride-acrylic ester copolymer	21 d	1.10×10^7	-	[61]
Micaceous Iron Oxide	Bisphenol A type epoxy resin	2 h	1.00×10^{11}	-	[62]
		16 d	1.10×10^5		
SiO ₂ nanoparticles	MTMS sol-gel	7 d	1.27×10^5	35 d	[63]
Zinc Phosphate	Epoxy resin	350 h	1.98×10^9	2500 h	[64]
		2500 h	5.31×10^8		
Self-doped nano-polyaniline	Epon 1001	1000 h	7.12×10^8	-	[65]
		1800 h	2.01×10^7		

Table S5 Diffusion coefficients of different corrosive media in different coatings.

Coatings	Diffusion coefficient, D ($\times 10^{-11} \text{ m}^2 \text{ s}^{-1}$)		
	Cl ⁻	H ₂ O	O ₂
EP	19.02	51.09	47.98
LDH-DE/EP	8.31	37.87	35.37
TA/LDH-DE/EP	5.29	25.83	23.86
TA/8-HQ@LDH-DE/EP	3.78	14.09	11.35

Table S6 FFV results of different coatings probed by different corrosive media.

Coatings	FFV (%)		
	Cl ⁻	H ₂ O	O ₂
EP	13.73	19.85	20.65

LDH-DE/EP	6.15	13.51	13.88
TA/LDH-DE/EP	4.18	7.59	8.07
TA/8-HQ@LDH-DE/EP	3.18	6.31	6.97

Table S7 Binding energies of TA-Fe and 8-HQ-Fe ionic complexes.

Chelation System	E_{ab} (Hartree)	E_a (Hartree)	E_b (Hartree)	E_{ad} (eV)
TA-Fe ²⁺	-2817.3898	-2414.3789	400.0891	-2.9218
8-HQ-Fe ²⁺	-2773.8216	-1185.9136	400.0891	-1.9053