Facile Construction of Self-Healing Polydopamine-Based Composite Coating Protection of Copper From NaCl Solution

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Developing a sufficient composite organic inhibitor coating on the surface of metals is a promising strategy to improve the protection capability of metal materials from corrosive media. In this study, dopamine is polymerized into a polydopamine coating on a copper surface by embedding 8-hydroxyquinoline (denoted as PDA@8-HQ). The formation mechanism of PDA@8-HQ on the surface of copper is confirmed by X-ray photoelectron spectroscopy, Fourier transform infrared reflectance, and Raman methods. Electrochemical and field emission scanning electron microscopic results show that the PDA@8-HQ coating made with the addition of 8-HQ was 0.02 M and had the greatest inhibition efficiency (99.1%). When the optimal composite coating is damaged by external forces, self-healing capability could be obviously found due to generating insoluble complex species between corrosive products of copper ions and 8-HQ and the salt solution in the damaged region. This study provides feasibility for the construction of functional corrosion inhibitors on the metal surface.

Keywords: copper, polydopamine, 8-hydroxyquinoline, self-healing, inhibition of corrosion

INTRODUCTION

Nowadays, various metals, such as magnesium alloys, aluminum, carbon steel, and copper, are used in navigation and industrial fields (Jing et al., 2018; Wan et al., 2018; Feng et al., 2020; Zhang et al., 2021). Among them, copper, with its perfect mechanical workability, high strength at low temperature, good availability, excellent eminent electrical and thermal conductivity, has been widely applied in the fields of condenser pipes of ships, civilian pipes, and coastal power plant heat exchangers (Albinia et al., 2018; Qianga et al., 2018). However, as an active metal, copper tends to be corroded in the environment, especially in media containing chloride ions (Cl\textsuperscript{-}). Therefore, for preventing such corrosion, many anticorrosion methods have been developed, including a sacrificial cathode, chromate conversion coatings, self-assembly monolayers (SAMs), chromate-free corrosion inhibitors, and organic–inorganic hybrid coatings (Tavandashti et al., 2016; Grigoriev et al., 2017; Hou et al., 2017; Qian et al., 2017; Xu et al., 2018), among which organic barrier coatings have gained great interest due to their retention of properties of the metal component (Nestorson et al., 2007).

Organic polymer coatings are explored extensively due to their stability, low cost, and good mechanical strength (Jiang et al., 2013). Dopamine (DA) could form polydopamine (PDA) coating by self-polymerization, which easily attaches onto the surface of materials (Zhang Z et al., 2013; Chou et al.,...
However, in corrosive suppression field, some cracks in the PDA coating formed during self-polymerization would result in metal corrosion in chloride ion environments. Additionally, metals with PDA coating used in thermal cycling or damaged by mechanical scratch would increase coating crack and even peel off from the substrate (Li et al., 2017). Therefore, enforcement of PDA coating by introducing inhibitors is an alternative way.

Inhibitors entrapped into composite coating could diffuse out of coating to heal the cracks produced by external force factors (Zhao et al., 2019; Xu et al., 2021) and such composite coating is known as “smart” coating. The “smart” coating especially means that the damaged area can be self-repaired (Bhzadnasab et al., 2017). In the literature, some methods were reported to fabricate self-healing films: 1) electrospun coaxial fiber (Cheng et al., 2018), 2) ion-exchange organic resins (Zhao et al., 2018), 3) sol–gel (Caldas et al., 2017), 4) layered double hydroxides, 5) hollow SiO₂ (Chen et al., 2015), and silica/polymer hybrid nanotubes (Li et al., 2017). Typically, self-healing could be achieved via the following pathway: the self-healing coating containing linseed oil-loaded nanocapsules, potassium ethyl xanthate, benzotriazole (Mahmoudian et al., 2018), 1H-benzotriazole-loaded mesoporous silica sol–gel coating (Li et al., 2019), micro-arc oxidation/polymethyltrimethoxysilane composite coating (Cui et al., 2017), and polymer coating containing healing agent and microencapsulated catalyst. In view of those strategies, tedious preparation procedures are unavoidable, and the optimization of the corrosion inhibitor content and self-healing efficiency should be considered (Sumerlin, 2018).

Recently, in previous work, a study on functionalized multi-walled carbon nanotube-reinforced coating for metal protection was conducted (Jiang et al., 2021). Carbon nanotubes (CNT), due to their high specific surface area, good corrosion inhibition ability, good thermal stability, and good mechanical performance, were added in PDA coating, which exhibited better corrosion inhibition efficiency of 98.8% than pure PDA coating. The promising protection was probably owing to a strong interaction between PDA and functionalized CNT via hydrogen bonds, enforcing passive coating in a uniform and dense way. In this work, 8-hydroxyquinoline (8-HQ) as an effective inhibitor for metal corrosion in chloride solutions has been validated (Daradmare et al., 2016). We carefully study the possibility of embedding 8-HQ into PDA coating to fill the coating defects to improve inhibition efficiency. In Scheme 1, the self-healing procedure of the PDA@8-HQ coating at the copper surface is illustrated. When such coating is damaged by external forces, the inhibitor in the composite coating will be exposed. Free copper (II) ions will electrostatically adsorb (Gerengi et al., 2016) with 8-HQ and complex to repair the cracks caused by external factors, and then 8-HQ will complex with copper (II) to heal the cracks caused by external force factors, which forms clathrate of bis(8-hydroxyquinoline) copper [Cu (HQ)₂] (Zhang K et al., 2013), as indicated in Supplementary Figure S1B.

**EXPERIMENT**

**Experimental Method**

Dopamine hydrochloride (98 wt.% purity), Tris(hydroxymethyl) aminomethane (99.8% purity), 8-hydroxyquinoline (8-HQ, 98 wt.% purity), and ethanol (AR) were purchased from Sigma-Aldrich Corporation. Hydrochloric acid (AR) and sodium chloride (AR) were obtained from Shanghai Richjoint chemical reagents co., Ltd.

**Pretreatment of Copper Electrode**

Teflon sealed copper rod (99.999 wt.%) with an area of 0.0314 cm² was used as the observed electrode. First, to remove the oxide/hydroxide layer, the copper electrode was ground with 500- and 1,000-grit SiC papers. Then, 0.3 µm Al₂O₃ was used to polish the electrode surface. Finally, the polished copper surface was rinsed with deionized (DI) water (18.2 MΩ cm), pure ethanol, and deionized water successively to remove the loose oxides and alumina residue.

**Surface Modification**

1) The copper electrode was immersed into 2 mg ml⁻¹ dopamine in 100 ml Tris–HCl (pH = 8.5) buffer solution for 12 h at room temperature. DA is therefore self-polymerized onto the copper surface, which is beneficial to the formation of a uniform and dense coating. The copper electrode with PDA coating, recorded
as PDA@Cu in the following text, was first rinsed with deionized water and then air-dried. The self-polymerization process of DA is shown in Supplementary Figure S1A.

2) The electrode was immersed in 0.02 M 8-HQ anhydrous ethanol solution for 12 h, rinsed with DI water, air-dried, and recorded as 0.02 M 8-HQ@Cu.

3) After that, 0.2 g DA was dissolved in 100 ml Tris–HCl (pH = 8.5) buffer with magnetic stirring at room temperature. Following that, 20 ml 8-HQ (with different concentrations) anhydrous ethanol solution was slowly added to dopamine solution under constant stirring. The final electrode (PDA@0.02M 8-HQ@Cu) was obtained after the bare copper electrode was immersed in the mixture solution for 12 h at room temperature.

Surface Characterization
The composition of the coating was characterized using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe,
It provided 1,486.6 eV photons using an Al Ka X-ray source (40 W, 15 KV). The test voltage and the base pressure of the analysis chamber were set at $6 \times 10^{-7}$ Pa and $2 \times 10^{-8}$ Pa, respectively. The coatings of PDA@Cu and PDA@0.02M 8-HQ@Cu were scraped off from the copper surface to conduct structural characterization by FTIR (Thermo Fisher Nicolet iS5, United States). The FTIR spectral range of 500–4,000 cm$^{-1}$ was recorded with 4 cm$^{-1}$ resolution in the transmission mode.

Raman spectra were collected using a confocal micro-Raman spectrometer (Super LabRam II system, Dilor, France). The laser and detector were 632.8 nm He-Ne laser and multichannel air-cooled 1,024 × 800 pixels charge-coupled device, respectively. The laser power, pinhole, and slit for Raman measurements were set at 5 mW, 1,000 μm, and 100 μm, respectively. Each Raman spectrum was acquired by 10 s three times and was calibrated using a silicon line (519.2 cm$^{-1}$).

The morphologies of electrodes were taken at 5 kV acceleration voltage by scanning electron microscopy (SEM, Hitachi S-4800).

### Electrochemical Test

To observe the electrochemical behaviors of the electrodes with coatings, by using a VersaSTAT4 electrochemical workstation (AMETEK Princeton Applied Research), OCP, EIS, and Tafel polarization curves were measured in 3.5 wt.% NaCl aqueous solution. A conventional three-electrode system was used, with copper, Pt wire, and saturated calomel electrode (SCE) as the working, counter, and reference electrodes. In detail, the electrodes were kept in the NaCl solution for 10,000 s before EIS tests to obtain a steady state of OCP. The EIS experiment was carried out in the range from 100 kHz to 0.01 Hz with an AC amplitude of 10 mV. The electrochemical polarization curve was acquired at an open-circuit voltage of OCP ± 0.25 V (vs. SCE) with a scan rate of 1 mV s$^{-1}$.

### Evaluation of the Self-Healing Properties

Bare copper, PDA@Cu, 8-HQ@Cu, and PDA@8-HQ@Cu specimens were scratched to expose the metallic substrates by using a ceramic knife (Analytik Jena). The scratched specimens were immediately immersed in 3.5 wt.% NaCl corrosive solution. The scratched portions of copper electrodes with and without treatment of corrosive media were observed using FE-SEM (Hitachi S-4800) and energy-dispersive X-ray (EDS) microanalysis (Hitachi S-4800).

Bare Cu and modified coppers were scratched and corroded in 3.5 wt.% NaCl solution for 10 h. Then linear sweep voltammetry (LSV) was performed by a VersaSTAT4 electrochemical workstation to evaluate self-healing behavior in three-electrode electrochemical cells. The potential range was from 0 to 1.0 V, and the scan rate was set at 50 mV/s (Bernsmann et al; Park and Braun., 2010, 2011; Johansen et al., 2012).

### TABLE 1

| Sample          | Bond content (at%) |
|-----------------|--------------------|
|                 | C = C  | C-C  | C-N  | C-O  | C = O |
| PDA@Cu          | 20.69  | 22.94| 21.73| 18.71| 15.93 |
| PDA@8-HQ@Cu     | 22.60  | 24.03| 19.39| 20.04| 13.94 |

### FIGURE 3

Open circuit potential versus time of different copper samples recorded in 3.5 wt.% NaCl aqueous solution (The error means a standard deviation of three measurements. OCPs of bare Cu, PDA@Cu, and concentration of 8-HQ in 0.005 M, 0.01 M, 0.015 M, 0.02 M, and 0.025 M are $-0.209 \pm 0.003$, $-0.196 \pm 0.002$, $-0.202 \pm 0.004$, $-0.198 \pm 0.003$, $-0.191 \pm 0.003$, $-0.172 \pm 0.002$, and $-0.187 \pm 0.001$ mV (vs. Ag/AgCl, 3 M KCl), respectively).
RESULTS AND DISCUSSION
Composition of Surface
The successful preparation of PDA@0.02M 8-HQ@Cu is confirmed by XPS and ATR-FTIR. Figures 1A, B show C 1s and N 1s XPS spectra of PDA@Cu and PDA@0.02M 8-HQ@Cu. From Figure 2, the contents of various C species are given in detail in Table 1. Some obvious differences could be found in C=C, C-C, C-N, C-O, and C = O groups after the introduction of 8-HQ, for PDA@0.02M 8-HQ@Cu in comparison with PDA@Cu. Direct evidence of the existence of 8-HQ in the composite coating could be offered via the comparison of the N 1s spectra. As shown in Figure 2C, N-C (399.7 eV) and N-H (400.9 eV) groups are attributed to PDA modified at the Cu surface, while in Figure 2D, the appearance of the C = N (398.7 eV) group in PDA@0.02M 8-HQ@Cu indicates the successful dopant of 8-HQ into PDA coating.

To further ascertain the structure of the coating, the FTIR experiment was conducted. As shown in Figure 1, the FTIR spectrum of 8-HQ presents a peak of C-H stretching at 3057 cm⁻¹, two bands at 1287 and 1274 cm⁻¹ correspond to C-N stretching, and a peak at 1580 cm⁻¹ is due to C = N stretching (Luo and Mather, 2013; Mahmoud et al., 2009), and the peaks at 1222 and 1206 cm⁻¹ are also from C-OH stretching of 8-HQ (Daradmare et al., 2016). All corresponding bands are observed in the FTIR spectrum of PDA@0.02M 8-HQ coating. Additionally, as compared with the FTIR spectrum of PDA, a new band at 1613 cm⁻¹ occurring in the FTIR spectrum of PDA@0.02M 8-HQ coating is assigned to the superposition of phenyl C = C stretching (Liu et al., 2013), and intermolecular hydrogen bonds in PDA present a broad band in the 3000- to 3400 cm⁻¹ region (Jiang et al., 2013). The previous FTIR investigation depicts the successful formation of a composite coating of PDA and 8-HQ at the copper surface.

Similarly, the Raman experimental results could also show the coating formation. From Supplementary Figure S2, Raman spectra of PDA@0.02M 8-HQ@Cu present a peak at 950 cm⁻¹ from 8-HQ and two peaks at 1382 and 1603 cm⁻¹ from PDA.

Open Circuit Potential
Recorded in 3.5 wt.% NaCl solution, Figure 3 shows the curves plotted by open circuit potential (OCP vs. SCE) versus time for bare copper, PDA@Cu, and different PDA@8-HQ@Cu formed by changing the amount of 8-HQ. OCPs of bare Cu, PDA@Cu, and PDA@8-HQ@Cu with different concentrations of 8-HQ (i.e., 0.005 M, 0.01 M, 0.015 M, 0.02 M, and 0.025 M) are −0.209 ± 0.003, −0.196 ± 0.002, −0.202 ± 0.003, −0.198 ± 0.003, −0.191 ± 0.003, −0.172 ± 0.002, and −0.187 ± 0.001 mV, respectively. Obviously, the low OCP value of PDA@Cu is due to the defects in PDA coating, which could be observed in the SEM image (Supplementary Figure S3). From another aspect, some cracks in the PDA coating formed by self-polymerization would result in the occurrence of metal corrosion in chloride ions. By introducing an inhibitor (8-HQ) to synthesize a composite coating, the PDA coating with 8-HQ at the copper surface could dramatically prevent the attack of chloride ions, and the OCP value is relatively higher due to the defects filled by 8-HQ. In Figure 3, the OCP values first shift to the anodic direction and then to the cathodic direction with the increasing 8-HQ concentration. The RSD results in Figure 3 are acquired by three measurements.

Due to external factors, the inhibitor in the composite coating will be exposed, and the free copper (II) ions will electrostatically adsorb with 8-HQ and complex to repair the cracks caused by external factors. Then, 8-HQ will complex with copper (II) to heal the cracks caused by external force factors. The test results showed that the corrosion inhibition effect of the coating is bad at low concentrations. The optimal concentration of 8-HQ to stuff the defects in the coating is 0.02 by observation of OCP at a more positive value, presenting the best anticorrosion ability. When a lower concentration of 8-HQ was used, the coating defects could not be filled completely, and when the 8-HQ concentration was

| Sample            | Ecorr (V vs. SCE) | icorr (µA cm⁻²) | β⁺ (V dec⁻¹) | β⁻ (V dec⁻¹) | η (%) |
|-------------------|-------------------|-----------------|--------------|--------------|-------|
| Bare copper       | 0.191 ± 0.002     | 0.776 ± 0.005   | 10.7 ± 0.86  | 23.1 ± 1.12  | —     |
| PDA@Cu            | 0.204 ± 0.003     | 0.129 ± 0.003   | 17.0 ± 1.51  | 18.7 ± 1.67  | 83.38 |
| PDA@0.005M 8-HQ@Cu| 0.215 ± 0.004     | 0.089 ± 0.004   | 11.6 ± 0.79  | 27.4 ± 0.98  | 88.53 |
| PDA@0.01M 8-HQ@Cu | 0.227 ± 0.003     | 0.044 ± 0.002   | 19.6 ± 0.94  | 37.6 ± 1.42  | 94.33 |
| PDA@0.015M 8-HQ@Cu| 0.201 ± 0.005     | 0.023 ± 0.003   | 49.3 ± 2.72  | 63.7 ± 2.71  | 96.78 |
| PDA@0.02M 8-HQ@Cu | 0.184 ± 0.003     | 0.0071 ± 0.002  | 37.4 ± 1.73  | 97.2 ± 1.85  | 99.09 |
| PDA@0.025M 8-HQ@Cu| 0.197 ± 0.005     | 0.0557 ± 0.004  | 21.3 ± 1.67  | 49.6 ± 2.98  | 92.82 |
excessive, 8-HQ would precipitate in the crystal form during the reaction, which also affected the integrity of the coating.

**Electrochemical Polarization**

The potentiodynamic polarization curves (Figure 4) of the bare and modified copper electrodes were acquired in 3.5 wt.% NaCl aqueous solution. The resultant electrochemical parameters are listed in Table 2. As described in the literature (Amin and Khaled., 2010; Yu et al., 2010; Li et al., 2011; Gerengi et al., 2016), copper corrosion reactions in chloride could be remarked as follows:

The anodic dissolution reactions are given as follows:
The cathodic oxygen reduction reaction is given as follows:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-.
\]  

By Tafel line extrapolation, the corrosion current density \((j_{\text{corr}})\), corrosion potential \((E_{\text{corr}})\), anodic Tafel slopes \((\beta_a)\), and cathodic Tafel slopes \((\beta_c)\) could be obtained. The \(j_{\text{corr}}\) value of the coated coppers is smaller than that of bare copper. The lowest \(j_{\text{corr}}\) could be reached at PDA@0.02M 8-HQ@Cu, which shows a decrease in magnitude by two orders, compared to bare copper (from 0.776 to 0.0071 µA). The results also suggest that the inhibition efficiency of the composite coating with 0.02 M 8-HQ exhibits the greatest resistance to salt corrosion, and the inhibition efficiency could reach 99.09%. In addition, all coatings retard both the cathodic and anodic reactions to some extent, and the differences in \(\beta_c\) are less noticeable than \(\beta_a\). This indicates that after modified copper surface with PDA or PDA@8-HQ, the reduction of dissolved oxygen and the diffusion of CuCl$_2^-$ are diminished (Zucchi et al., 2004).

### Electrochemical Impedance Spectroscopy

To evaluate the protective ability of the composite coating for copper, EIS is an effective method (King et al., 2014). Supplementary Figure S4 shows the Nyquist plots of the coated copper electrodes in 3.5 wt.% NaCl solution, and the inset plot shows that of the bare copper. A capacitive loop in the high-frequency range could indicate the solution resistance, and a straight line in the low-frequency range, Warburg impedance, is associated with the diffusion of CuCl$_2^-$ (Babouri et al., 2015). After modification by PDA and PDA@8-HQ at the copper surfaces, in both EIS spectra, the Warburg impedances disappear and the radius of the capacitive loops increases. PDA@0.02M 8-HQ@Cu presents the highest impedance modulus.

In the Bode plots in Figure 5A, the impedance value at low frequency \(|Z|_{0.01\text{Hz}}\) increases from 3.48 to 5.16 with respect to bare copper. In the phase angle plots of Figure 5B, bare copper, PDA@Cu, and PDA@8-HQ@Cu have two time constants. PDA@0.02 M 8-HQ@Cu shows the maximum phase angle, manifesting the best inhibition efficiency. The result is in good consistency with that of potentiodynamic polarization.

For better understanding of the corrosion mechanism, ZsimpWin software was used to fit impedance spectra. The equivalent circuit model shows the minimum error and chi-square value \((\chi^2)\) less than $1 \times 10^{-3}$. The fitted electrical circuits are shown in Figure 6, and the corresponding electrochemical parameters are listed in Table 3. The most suitable fitting circuit model for bare copper is $R(Q\{R\{QR\}\})$, while the equivalent circuit model of $R(Q[R(QR)])$ is picked out for PDA@Cu. Additionally, $R(QR)(QR)$ is a better mode for fitting the PDA@8-HQ coating. In the equivalent circuits, $R_s$ stands for NaCl solution resistance, and $R_{ct}$ and $R_p$ represent charge transfer resistance and the resistance of the film, respectively. Constant phase elements ($Q_c$ and $Q_f$) are with respect to copper oxide, PDA coating, and PDA@8-HQ coating. $W$ is Warburg impedance. The Q impedance is defined as $Z_Q = Y_0^{-1} (j\omega)^{-n}$ (Shi et al., 2017), in which $Y_0$ is the values of $Q$, $j$ is the imaginary number, $\omega$ ($\omega = 2\pi f$) is the angular frequency, and $n$ is the phase ($-1 \leq n \leq 1$), which is related to the inhibitor adsorption, surface inhomogeneity, and porous layer formation. When $n$ is $-1$, 0, 0.5, and 1, the Q

\[
\begin{align*}
\text{Cu} &\rightarrow \text{Cu}^+ + e^-, \\
\text{Cu}^+ + \text{Cl}^- &\rightarrow \text{CuCl}, \\
\text{CuCl} + \text{Cl}^- &\rightarrow \text{CuCl}_2 \\
\text{CuCl}_2^- &\rightarrow \text{Cu}^{2+} + 2\text{Cl}^- + e^-.
\end{align*}
\]
**FIGURE 8 | (A):** SEM image of the scratched PDA@0.02M 8-HQ@Cu and EDS spectrogram. (B): SEM image of the scratched PDA@0.02M 8-HQ@Cu and high magnification, immersed in 3.5 wt.% NaCl aqueous solution for 10 h (corrosion time) at 25°C, and EDS spectrogram.
represents inductance, resistance, Warburg impedance, and capacitance, respectively. As seen in Table 3, the n value of modified samples ranges from 0.5 to 1, meaning the relatively slow corrosion process (Li et al., 2014).

As for blank copper, $R_f$ and $Q_f$ are attributed to the inevitable layer of corrosion products (Refait et al., 2020). Nevertheless, diffusion in such a relatively thin layer then becomes possible, resulting in the presence of $W$. As for the PDA-modified copper

**TABLE 4** Anticorrosion performance obtained from potentiodynamic polarization curves recorded with the self-healing tests on PDA@Cu and PDA@0.02 M 8-HQ@Cu samples.

| Sample                  | $\bar{E}_{corr}$ (V vs. SCE) | $\bar{i}_{corr}$ (µA cm$^{-2}$) | $\bar{p}_{c}$ (V dec$^{-1}$) | $\bar{p}_{a}$ (V dec$^{-1}$) | $\eta$ (%) |
|-------------------------|-------------------------------|---------------------------------|-------------------------------|-------------------------------|------------|
| Bare copper             | 0.191 ± 0.002                 | 0.776 ± 0.005                  | 10.7 ± 0.86                   | 23.1 ± 1.12                   | 93.38      |
| PDA                     | 0.204 ± 0.004                 | 0.129 ± 0.003                  | 17.0 ± 1.51                   | 18.7 ± 1.67                   | 93.50      |
| Scratched               | 0.222 ± 0.001                 | 0.291 ± 0.003                  | 21.6 ± 0.93                   | 14.1 ± 0.74                   | 93.60      |
| Self-healing 10 h       | 0.223 ± 0.002                 | 0.296 ± 0.002                  | 21.0 ± 0.79                   | 11.8 ± 0.82                   | 93.90      |
| Self-healing 20 h       | 0.225 ± 0.003                 | 0.447 ± 0.004                  | 18.6 ± 0.86                   | 16.7 ± 1.01                   | 94.00      |
| PDA@0.02M 8-HQ          | 0.184 ± 0.003                 | 0.007 ± 0.008                  | 37.4 ± 1.73                   | 97.2 ± 1.85                   | 94.10      |
| Scratched               | 0.189 ± 0.002                 | 0.268 ± 0.002                  | 21.9 ± 0.89                   | 39.2 ± 0.79                   | 94.20      |
| Self-healing 10 h       | 0.185 ± 0.001                 | 0.047 ± 0.005                  | 19.5 ± 0.99                   | 37.8 ± 0.93                   | 94.30      |
| Self-healing 20 h       | 0.184 ± 0.003                 | 0.003 ± 0.004                  | 19.6 ± 0.82                   | 36.8 ± 1.05                   | 94.40      |

**TABLE 5** Reproducibility of anticorrosion performance obtained from EIS measurements recorded with the self-healing tests on five different PDA@0.02M 8-HQ samples.

| PDA@0.02M 8-HQ@Cu | $R_s$ (Ω cm$^2$) | $R_f$ (Ω cm$^2$) | $Q_1$ $Y_0$ $10^{-4}$ | $n_1$ | $Q_2$ $Y_0$ $10^{-4}$ | $n_2$ | $R_{ct}$ (Ω cm$^2$) | $R_p$ | RSD (%) |
|-------------------|------------------|------------------|------------------------|-------|------------------------|-------|----------------------|-------|---------|
| 1                 | 1.672            | 2.743            | 2.557                  | 0.661 | 9.112                  | 0.5195| 327.58               | 3,070.58| 2.69    |
| 2                 | 1.885            | 2.413            | 4.655                  | 0.6764| 2.145                  | 0.6721| 570.4                | 2,983.4| 9.10    |
| 3                 | 1.235            | 2.938            | 3.598                  | 0.7124| 3.493                  | 0.7655| 261.85               | 3,199.85| 2.20    |
| 4                 | 1.899            | 2.590            | 2.589                  | 0.6893| 3.966                  | 0.6254| 452.79               | 3,042.79| 2.20    |
| 5                 | 1.537            | 2.632            | 2.887                  | 0.6989| 2.717                  | 0.7559| 499.5                | 3,131.15| 2.20    |
SELF-HEALING BEHAVIOR

SEM Observations

Figure 7 shows FE-SEM images of copper with and without PDA or 8-HQ coatings, scratched by external forces, which were taken before and after corroded in 3.5 wt.% NaCl aqueous solution for 10 h. In Figures 7B,D, after immersion, there are many pitting corrosions that occurred at the scratched bare copper and the scratched 0.02M 8-HQ@Cu surface, and the visible corrosion products around the scratched spots indicate severe corrosion. Much seriously, in Figure 7F, the PDA coating has partly peeled off from the copper surface after long-term immersion in NaCl media. Obviously, the protection efficiencies of copper from corrosive solution by only PDA coating or 8-HQ are not satisfactory. Figure 8A shows SEM images and EDS results recorded before immersion of the scratched PDA@0.02M 8-HQ@Cu in salt solution. The exposure of copper in the scratched portion of PDA@0.02M 8-HQ@Cu could be visible.

In Figure 8B of scaled SEM images, after the scratched PDA@0.02M 8-HQ@Cu in 3.5 wt.% NaCl solution for 10 h, some nanorods produced in the vicinity of the scratched trace could be found, and the EDS result indicates that the nanorods are mainly composed of O, N, C, and Cu elements. Supplementary Figure S5 shows the section views of the PDA@0.02M 8-HQ@Cu. After immersion in 3.5 wt.% NaCl aqueous solution for 10 h, nearly no corrosion occurred in the scratched portion due to the self-healing ability of composite coating. It shows that when the coating is damaged by external forces, 8-HQ embedded in the PDA coating would combine with copper ions through electrostatic attraction, forming insoluble clathrate of bis(8-hydroxyquinoline) copper [Cu (HQ)₂]. The preeminent self-healing ability of such PDA@0.02M 8-HQ composite coating will also be validated by following an electrochemical experiment.

Electrochemical Test

Potentiodynamic polarization was used to characterize self-healing property. PDA@Cu and PDA@0.02M 8-HQ@Cu were scratched with a knife, and then the scratched coatings were immersed in 3.5 wt.% NaCl solution for 0 h, 10 h, and 20 h. As shown in Figures 9A,B and Table 4, compared to the intact PDA@Cu and PDA@0.02M 8-HQ@Cu, jcorr values of both scratched coatings increased. However, Jcorr value of the scratched PDA@Cu sample kept increasing with increasing immersion time, indicating further corrosion in NaCl aqueous solution. By contrast, for PDA@0.02M 8-HQ@Cu, jcorr value remarkably decreased (down to 0.003 μA cm⁻²) as soaking time increased, and after self-healing for 20 h, the inhibition efficiency of the scratched PDA@0.02M 8-HQ@Cu recovered to the original level of the unscratched one.

Figures 9C,D show the Bode plots of self-healing tests of PDA@Cu and PDA@0.02M 8-HQ@Cu. At the beginning stage, the impedance values at low frequency for scratched PDA@Cu and PDA@0.02M 8-HQ@Cu reduce an order of magnitude compared to undamaged coatings. Similarly, after self-healing for 20 h, the impedance value of scratched PDA@0.02M 8-HQ@Cu increased to the same level as the unscratched coating, hinting that the scratches have been repaired by 8-HQ molecules. By contrast, in the case of scratched PDA@Cu, the impedance value decreased with the time undergoing. From Table 5, EIS measurements with RSD about 2.69% repeated for five batches of scratched samples reveal excellent reproducibility. Figure 9E shows OCP (vs. SCE) curves for scratched PDA@Cu and scratched PDA@0.02M 8-HQ@Cu in 3.5 wt.% NaCl solution over the immersion time. Both OCP values (vs. SCE) of scratched PDA@Cu and scratched PDA@0.02M 8-HQ@Cu present a sharp fall in the first 3 h, indicating corrosion occurrence in the cracks by the penetration of the corrosive media. After 3 h, OCP (vs. SCE) of scratched PDA@Cu remained decreased, while OCP (vs. SCE) of scratched PDA@0.02M 8-HQ@Cu increased due to the self-healing behavior. After 12 h, the OCP value of scratched PDA@0.02M 8-HQ@Cu coating reached 181 mV (vs. SCE), which was close to the undamaged coating (ca. 172 mV). The self-healed coating exhibited a stable protection performance for the copper substrate after immersion in salt solution for 20 h.

CONCLUSION

In summary, a facile strategy to prepare a protection coating with self-healing capability was proposed. We first constructed a composite coating at the copper surface by embedding inhibitor of 8-HQ into the PDA coating by using the one-step method. Under an optimal formation of the composite coating by using 8-HQ at 0.02 M, the suppression efficiency of about 99.1% can be reached. PDA@0.02M 8-HQ@Cu not only showed the efficient inhibition of corrosion but also demonstrated the self-healing ability in case of mechanical damage. By scratching PDA@0.02M 8-HQ@Cu electrode, the inhibitor in the composite coating will be exposed, and Cu (II) will electrostatically adsorb with 8-HQ and complex to seal the cracks caused by scratching to produce the complication, which sufficiently inhibits corrosion occurring in the scratched trace. After 20 h of self-healing, the inhibition efficiency reached 99.61%.

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DATA AVAILABILITY STATEMENT
The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS
JF and WC: conceptualization and writing/original draft preparation; YJ and SL: investigation and numerical calculations; and HY and YY: writing—review and editing. All the authors contributed to the article and approved the submitted version.

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SUPPLEMENTARY MATERIAL
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