Corrosion Monitoring Effect of Rhodamine-Ethylenediamine on Copper Relics under a Protective Coating

Xing-Ling Tian,* Chao Feng, and Xu-Hui Zhao*

ABSTRACT: Fluorescence spectroscopy is a common technique used to monitor early metallic corrosion. The fluorescence response characteristics of rhodamine-ethylenediamine toward Cu²⁺ have been studied using fluorescence and infrared spectroscopy. Fluorescence microscopy and electrochemical impedance spectroscopy were used to study the monitoring effect of rhodamine-ethylenediamine on the corrosion of copper relics protected by an epoxy coating. The results showed a strong fluorescent response and selectivity toward Cu²⁺ that existed using rhodamine-ethylenediamine. Early metallic corrosion of copper relics can be effectively monitored upon adding 0.8 wt % rhodamine-ethylenediamine to an epoxy coating. When the soaking time was increased, the fluorescence intensity of the fluorescent area on the coating became stronger. In addition, the area of the luminous coating reached ∼0.06 mm² and the area of corrosion under the protective coating was ∼0.008 mm², which was about 1/10 of the fluorescence area observed on the coating.

1. INTRODUCTION

Protective coatings are one of the effective strategies used to protect copper relics. However, copper relics protected by the coating can still be corroded. It is of great significance to monitor for early corrosion before any obvious corrosion occurs. Using corrosion monitoring, the regions of early corrosion can be identified, which contribute to the timely detection of corrosion and its corresponding maintenance. Due to its high sensitivity and precise measurement, fluorescence spectroscopy can be used to evaluate and monitor the corrosion tendency and level more accurately. Moreover, because the protective coatings used for cultural relics are transparent, they are particularly suited to the use of fluorescence spectroscopy to monitor the levels of corrosion. Generally, corrosion monitoring using fluorescence spectroscopy can be divided into two categories: (i) the fluorescent probe can combine with H⁺ or OH⁻ to generate a new fluorescent material, which can be used to monitor the variation in the pH of local corrosion and reflect the degree of corrosion, such as 5,6-carboxyfluorescein and calcein. (ii) The fluorescent probe can coordinate with the metal ion and thereby generate a fluorescence effect, which can be used to monitor the variation in the concentration of the metal ion in the region of corrosion, such as quinolone.

Using a fluorescent probe, Buchler et al. have investigated the local corrosion in aluminum alloy 6061 and determined the distribution of the anode and cathode region, which provided a new method to study local corrosion. Sibi and Zong have studied the corrosion mechanism of aluminum alloy under the protective coating by adding several fluorescent probes to the coating. Using 8-hydroxyquinoline (8-HQ) as a fluorescent probe and an ultraviolet lamp as an excitation source, Bryant and Greenfield monitored the early corrosion under a protective coating. Furthermore, they also researched on the...
quenching effect of iron ions. Ju et al.\textsuperscript{12} have reported the corrosion monitoring selectivity of several fluorescent probes in the protective coating used for aluminum alloy. The results indicated that the corrosion response of the sol–gel film containing 8-HQ was more sensitive toward the aluminum substrate. The sol–gel film could be used to monitor early corrosion. Although many studies have suggested that fluorescence spectroscopy is available for monitoring metallic corrosion, most of them focus on light metal alloys, such as aluminum and magnesium. However, there are few reports on copper-based materials, to the best of our knowledge, especially no report on copper relics. Because the coating materials of copper relics are almost transparent, the application effect of this method will be more obvious. It is the first time to apply this method to evaluate coating materials on copper relics. In addition, the specific corrosion status of the metal substrate under a protective coating and an evaluation of the protective effect require further study.

In this work, rhodamine-ethylenediamine was chosen as a fluorescent probe. The fluorescence effects of rhodamine-ethylenediamine toward Cu\textsuperscript{2+} were analyzed using fluorescence spectroscopy. A combination of electrochemical impedance spectroscopy and fluorescence microscopy was used to study the relationship between the degree of metallic corrosion under the protective coating and the fluorescence intensity. Moreover, the feasibility of this system for the corrosion monitoring of copper relics using fluorescence spectroscopy is also discussed.

2. RESULTS AND DISCUSSION

2.1. Fluorescent Response Characteristics of Rhodamine-Ethylenediamine toward Cu\textsuperscript{2+}. Figure 1 shows the fluorescence spectra of the solutions of the rhodamine-ethylenediamine fluorescent probe in the presence of different concentrations of Cu\textsuperscript{2+}. The absorption peaks located at about 586 nm and the intensity of the absorption peak increased with the increment in the concentration of Cu\textsuperscript{2+}. When the Cu\textsuperscript{2+} concentration reached 200 μmol/L, the intensity reached the maximum value. When the concentration further increased, the fluorescence intensity decreased. The main reason for the increase in the fluorescence intensity was the formation of a ring opening structure when the rhodamine-ethylenediamine probe encountered Cu\textsuperscript{2+}. Moreover, the formation of more ring opening structures emitted stronger fluorescence.\textsuperscript{13–15} Nevertheless, with a further increase in the Cu\textsuperscript{2+} concentration, the polymerization of rhodamine-ethylenediamine with Cu\textsuperscript{2+} occurred, leading to the formation of an amorphous complex with a relatively low luminous emissivity. As a result, the fluorescence intensity did not increase obviously and even slightly decreased.\textsuperscript{14–16}

Figure 2 shows the FT-IR spectra of the samples obtained by drying rhodamine-ethylenediamine solutions with and without Cu\textsuperscript{2+}. The peaks observed at 1610, 1366, and 1221 cm\textsuperscript{-1} were attributed to the stretching vibrations of C=O, aryl C–N, and alky C–N in rhodamine-ethylenediamine, respectively.\textsuperscript{7–19} For the sample of rhodamine-ethylenediamine + Cu\textsuperscript{2+}, an absorption peak appeared at 1046 cm\textsuperscript{-1}, which is the stretching vibration peak of C–O, due to the new seven-membered ring formed by the ring opening of the lactam and Cu\textsuperscript{2+}. The carbonyl double bond of rhodamine-ethylenediamine was opened, and the peak intensity of 1689 cm\textsuperscript{-1} decreased significantly. This indicated that the spirolactam of rhodamine-ethylenediamine had been destroyed, and the ring opening conjugate structure was formed, as shown in Figure 3.\textsuperscript{20–23}

Figure 3. Schematic diagram of possible complexation of rhodamine-ethylenediamine with copper ions.

To further study the response characteristics of rhodamine-ethylenediamine to Cu\textsuperscript{2+}, 200 μmol/L Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Zn\textsuperscript{2+}, Ca\textsuperscript{2+}, Al\textsuperscript{3+}, Fe\textsuperscript{3+}, and other metal ions (added in the form of chloride) were added to 200 μmol/L rhodamine-ethylenediamine solutions, and their fluorescence spectra were measured. Figure 4 shows the fluorescence spectra of the rhodamine-ethylenediamine fluorescent probe in the presence of different metal ions. It can be seen that there was no obvious
fluorescence effect when Na⁺, K⁺, Mg²⁺, Zn²⁺, Ca²⁺, Al³⁺, and Fe³⁺ were added to the rhodamine-ethylenediamine solution. However, a fluorescence absorption peak at 586 nm was observed in the rhodamine-ethylenediamine solution containing Cu²⁺, suggesting the good selectivity of the rhodamine-ethylenediamine probe toward Cu²⁺, which was due to the fact that only Cu²⁺ among these tested metal ions can form the products with a fluorescence structure. Figure 5 shows a comparison of the fluorescence intensities of the rhodamine-ethylenediamine fluorescent probe in the presence of metal ions such as Na⁺, K⁺, Mg²⁺, Zn²⁺, Ca²⁺, Al³⁺, and Fe³⁺. When other metal ions were added, almost no effect on the fluorescence intensity of the rhodamine-ethylenediamine probe with Cu²⁺ was observed. This showed that, as a fluorescent chemical sensor for Cu²⁺, rhodamine-ethylenediamine exhibited a strong anti-jamming capability.

2.2. Corrosion Monitoring Effect. Figure 6 shows the fluorescence intensity of an epoxy coating containing different amounts of rhodamine-ethylenediamine after being soaked in a solution Cu²⁺ for 1.5 h. The amount of rhodamine-ethylenediamine increased to a certain value, Cu²⁺ in the solution formed the fluorescence products totally, and the fluorescence intensity reached a maximum value at this time. Thus, the amount of rhodamine-ethylenediamine added to the protective coating was selected to be 0.8 wt %.

The copper relic coated with an epoxy coating containing 0.8 wt % rhodamine-ethylenediamine was soaked in a 3.5% NaCl solution. An alternating current impedance test was regularly carried out. Moreover, the time and fluorescence intensity in which the fluorescent signal appeared were observed and recorded.

Figures 7 and 8 show the alternating current impedance spectra and fluorescence microscopy images of the coated sample, respectively. For the coated sample, the initial |Z|₀₀₀Ｈz value was close to 1 × 10⁹ Ω cm² and no fluorescence signal in the coating was observed under the fluorescence microscope, as shown in Figure 8a. Upon prolonging the soaking time, the impedance signal continued to decrease. After being soaked for 5 days, the |Z|₀₀₀Ｈz value decreased to 1 × 10⁸ Ω cm², but there was still no evident fluorescent signal in the protective coating and no obvious corrosion on the copper substrate. After 7 days, the |Z|₀₀₀Ｈz value was smaller than 1 × 10⁸ Ω cm². Under an ultraviolet lamp, a weak fluorescence in the protective coating was observed, as shown in Figure 8b. Using optical microscopy, no obvious corrosion spot was observed on the metallic surface of the coated sample. Thus, the fluorescent probe could be used to indicate corrosion on the metal substrate. When the coated sample was soaked continuously for 10 days, the |Z|₀₀₀Ｈz value further decreased. Meanwhile, the color of the fluorescent area on the coating gradually deepened, as shown in Figure 8c. When soaked up to 20 days, the |Z|₀₀₀Ｈz value decreased to 1 × 10⁷ Ω cm². In addition, the fluorescence intensity in the fluorescent area became stronger. Finally, it shows a macroscopic fluorescent area with stable luminescence and the area of the luminous coating was ~0.06 mm². The fluorescence microscopy image of the coated surface is shown in Figure 8d. Figure 9 shows the surface morphology of the copper substrate after removing the protective coating. The approximate size of the area of corrosion was 10³ μm, and the corrosion area was ~0.008 mm², which was approximately 1/10 of the fluorescent area observed on the coating. Therefore, the fluorescent probe possessed an excellent monitoring capability for early corrosion on a metal substrate.

(a) 2 h, (b) 7 days, (c) 10 days, and (d) 20 days.
3. CONCLUSIONS

(1) Rhodamine-ethylenediamine showed a strong fluorescent response and selectivity toward Cu$^{2+}$ as well as an excellent anti-jamming capability toward metal ions such as Na$^+$, K$^+$, Mg$^{2+}$, Zn$^{2+}$, Ca$^{2+}$, Fe$^{3+}$, and Al$^{3+}$.

(2) Early corrosion of metal under a protective coating was effectively monitored using an epoxy coating containing 0.8 wt % rhodamine-ethylenediamine. When the soaking time was increased, the fluorescence intensity of the fluorescent area on the coating became stronger. In addition, the area of the luminous coating reached ~0.06 mm$^2$ and the area of corrosion under the protective coating was ~0.008 mm$^2$, which was about 1/10 of the fluorescence area observed on the coating.

4. EXPERIMENT

4.1. Preparation of Coated Samples. In the experiments, a bronze substrate (60 mm × 50 mm × 0.5 mm) was used to simulate a copper relic. The protective coating used consisted of a two-component epoxy coating (the epoxy resin is 3EE101W, and the curing agent is 3EC150Y, which are produced by Tongde Chemical Co., LTD, in Foshan City). The epoxy resin was mixed with the curing agent in a 5:1 weight ratio under stirring for 10 min prior to use. The surface of the bronze sample was sanded to 600#, degreased with alcohol, dried by cold wind, and then coated with a protective coating by hand. The coating was about 30 microns thick.

4.2. Measuring Methods. Aqueous solutions of CuCl$_2$ at different concentrations were prepared. An appropriate amount of rhodamine-ethylenediamine was then added to prepare a mixed solution containing 200 μmol/L rhodamine hydrazide. The fluorescence spectra were measured using an F-7100 fluorescence spectrophotometer (Hitachi, Japan) and used to analyze the effects of the concentrations of Cu$^{2+}$ and other metal ions on the fluorescence intensity and the fluorescence intensity of coated samples. The excitation light source is a steady-state xenon lamp with a wavelength of 345 nm. The coated samples were placed on a solid sample support, and each sample was tested at least three times. The infrared spectra were recorded using a Fourier transform infrared spectrometer (TENSOR 27, Bruker, Germany). The powdered samples were obtained by drying the mixed solutions of the different fluorescent probes and metal ions at 100°C in an oven. The measuring range was 500−4000 cm$^{-1}$. Alternating current impedance spectroscopy was measured on an electrochemical workstation (PARSTAT 2273, Princeton, USA) using a three-electrode system. Platinum and calomel electrodes were used as the auxiliary and reference electrodes, respectively, while the copper specimens coated with the different fluorescent probes served as the working electrode. The effective area of the coating was 10 cm$^2$. The amplitude of the alternating current signal was 10 mV, and the frequency range was $10^{-2}$ Hz. The alternating current impedance tests were carried out in a 3.5 wt % NaCl solution. A metallographic and fluorescence microscope (HG-001, Old Polishing Instrument Factory) was used to observe the fluorescence micromorphology with an excitation light wavelength of 435 nm.

Figure 7. Electrochemical impedance spectra obtained for a bronze sample coated with epoxy resin containing rhodamine-ethylenediamine recorded in 3.5% NaCl solution. (a) Impedance modules and (b) phase angle.

Figure 8. Fluorescence microscopy images of a bronze sample coated with epoxy resin containing 0.8 wt % rhodamine-ethylenediamine after being soaked in a 3.5% NaCl solution for different times:

Figure 9. Superficial corrosion morphology of the bronze sample after removal of the protective coating.
**AUTHOR INFORMATION**

**Corresponding Authors**
Xing-Ling Tian — Chinese Academy of Cultural Heritage, Beijing 100029, China; orcid.org/0000-0003-1595-9997; Email: tianxirling1278@sina.com

Xu-Hui Zhao — Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China; Email: xzhao@mail.buct.edu.cn

**Author**
Chao Feng — Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsofme.0c02535

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The research is supported by the Independent Research Fund Project of the Chinese Academy of Cultural Heritage and the Major Project of State Administration of Cultural Heritage. We thank Prof. Lin Yuzhen for helpful conversations and Mr. Yang Ziran for assistance with samples and producing several of the figures.

**REFERENCES**

(1) Dhole, G. S.; Gunasekaran, G.; Singh, S. K.; Vinjamur, M. Smart corrosion sensing phenanthroline modified alkyd coatings. *Prog. Org. Coat.* 2015, 89, 8–16.

(2) Sibi, M. P.; Zong, Z. Determination of corrosion on aluminum alloy under protective coatings using fluorescent probes. *Prog. Org. Coat.* 2003, 47, 8–15.

(3) Xia, T. F.; Zhang, L.; Zhang, D. Q.; Gao, L. X. Detection of T91 steel corrosion with a Fe$^{3+}$-enhanced fluorescence probe. *J. Chem.* 2015, 654802.

(4) Jones, D. A.; Amy, P. S. A thermodynamic interpretation of microbiologically influenced corrosion. *Corrosion* 2002, 58, 638–645.

(5) Maia, F.; Tedim, J.; Bastos, A. C.; Ferreira, M. G. S.; Zheludkevich, M. L. Nanocontainer based corrosion sensing coating. *Nanotechnology* 2013, 24, 415502.

(6) Liu, X.; Spikes, H.; Wong, J. S. S. In situ pH responsive fluorescent probing of localized iron corrosion. *Corros. Sci.* 2014, 87, 118–126.

(7) Luo, L.; Liu, Z. H.; Chen, T. L. An optical chemical sensing membrane for the determination of pH. *Chin. J. Anal. Chem.* 2005, 4, 483–486.

(8) Rurack, K. Flipping the light switch ‘ON’—the design of sensor molecules that show cation-induced fluorescence enhancement with heavy and transition metal ions. *Spectrochim. Acta A* 2001, 57, 2161–2195.

(9) Li, J.; Lu, Y. A highly sensitive and selective Catalytic DNA Biosensor for Lead ions. *J. Am. Chem. Soc.* 2000, 122, 10466–10467.

(10) Büchler, M.; Watari, T.; Smyrl, W. H. Investigation of the initiation of localized corrosion on aluminum alloys by using fluorescence microscopy. *Corros. Sci.* 2000, 42, 1661–1668.

(11) Bryant, D. E.; Greenfield, D. The use of fluorescent probes for the detection of under-film corrosion. *Prog. Org. Coat.* 2006, 57, 416–420.

(12) Ju, P. F.; Zhao, X. N.; Xiong, L. L. Effects of fluorescent agent on sensitivity of corrosion monitoring of anticorrosion coatings on aluminum alloy. *China Surf. Eng.* 2018, 31, 116–125.

(13) Sun, C.; Chen, J.; Ma, H.; Liu, Y.; Zhang, J.; Liu, Q. A new Cu$^{2+}$-induced color reaction of a rhodamine derivative N-(3-carboxy)

acryloyl rhodamine B hydrazide. *Sci. China Chem.* 2011, 54, 1101–1108.

(14) Liu, Y.; Sun, Y.; Du, J.; Lv, X.; Zhao, Y.; Chen, M.; Wang, P.; Guo, W. Highly Sensitive and Selective Turn-on Fluorescent and Chromogenic Probe for Cu$^{2+}$ and ClO$^{-}$ Based on a N-Picolinyl Rhodamine B-Hydrade Derivative. *Org. Biomol. Chem.* 2011, 9, 432–437.

(15) Chen, X.; Ma, H. A selective fluorescence on reaction of spiro form fluorescein hydrazide with Cu (II). *Anal. Chim. Acta* 2006, 575, 217–222.

(16) Chen, X.; Baek, K.-H.; Kim, Y.; Kim, S.-J.; Shin, I.; Yoon, J. A selenolactone-based fluorescent chemodosimeter to monitor mercury/methylmercury species in vitro and in vivo. *Tetrahedron* 2010, 66, 4016–4021.

(17) Li, G.; Tao, F.; Wang, H.; Li, Y.; Wang, L. A novel reversible colorimetric chemosensor for rapid naked-eye detection of Cu$^{2+}$ in pure aqueous solution. *Sens. Actuators B Chem.* 2015, 211, 325–331.

(18) Sun, H.; Zhang, Z.; Meng, P. Catalytic oxidation of Rhodamine B in water by loaded ferric complex. *Text. Aux.* 2016, 33, 49–52.

(19) Pal, P.; Das, B.; Dadhich, P.; Achar, A.; Dhara, S. Carbon nanodot impregnated fluorescent nanofibers for in vivo monitoring and accelerating full-thickness wound healing. *J. Mater. Chem. B* 2017, 5, 6645–6656.

(20) Xu, Y.; Chen, Y. H.; Ding, L. One-pot microwave assisted synthesis of passivated fluorescent carbon dots for Fe(III) detection. *Chem. J. Chin. Univ.* 2018, 39, 1420–1426.

(21) Chen, B.; Dong, H. J.; Du, J. J.; Fan, J. L.; Peng, X. J. A colorimetric probe for copper ion in aqueous solution. *Sci. Sin. Chim.* 2014, 44, 1491–1498.

(22) Dujols, V.; Ford, F.; Czamik, A. W. A Long-Wavelength Fluorescent Chemodosimeter Selective for Cu(II) Ion in Water. *J. Am. Chem. Soc.* 1997, 119, 7386–7387.

(23) Wang, X. C.; Liu, X. D.; Yang, Y. L.; Shen, Q. H.; Luo, S. G.; Li, Q. Application of Rhodamine-Based Fluorescence Chemosensor in Heavy Metal Ions and Transition Metal Ions Detection. *Spectrosc. Spect. Anal.* 2000, 30, 2693–2699.