



Electrochemical and anti-corrosion properties of octadecanethiol and benzotriazole binary self-assembled monolayers on copper



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ABSTRACT

Self-assembled monolayers based on octadecanethiol ($C_{18}H_{37}-SH$) and benzotriazole (BTA) ($C_{18}H_{37}-SH\&BTA$ SAMs) were fabricated on copper surface, showing effective corrosion protection for the substrate. The self-assembled monolayers (containing the composite SAMs and the SAMs based on single $C_{18}H_{37}-SH$ or BTA) were characterized by surface enhanced Raman spectroscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and the results show that both $C_{18}H_{37}-SH$ and BTA are successfully self-assembled on copper surface, forming compact SAMs. The anti-corrosion performance of the SAMs was studied by potentiodynamic polarization and electrochemical impedance spectroscopy. It is revealed that the anti-corrosion performance of the binary ($C_{18}H_{37}-SH$ and BTA) composite SAMs is influenced by the assembling sequence. The $C_{18}H_{37}-SH\&BTA$ SAMs display the best anti-corrosion performance for copper with the highest charge transfer resistance of $5.0 \cdot 10^5 \Omega \text{ cm}^2$.

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1. Introduction

Copper (Cu) and its alloys, as a kind of structural and functional materials, are widely used in industrial and artistic manufacturing due to their excellent electrical and thermal conductivities, mechanical workability and shining appearance [1]. However, these Cu-based materials are often prone to corrosion in some media, such as atmosphere or aqueous solutions with high ionic concentration, especially chlorine [2]. When being exposed to these severe circumstances, copper will be corroded, which will deteriorate the performance and appearance of copper-based materials, it is therefore of great significance to seek for effective, low-cost and environmentally friendly techniques to prevent copper corrosion.

With regard to the protection of copper and its alloys, the generally employed method is to isolate the materials from the surrounding environment, including electroplating [3], coating [4–6], conversion films and employment of adsorptive corrosion inhibitor [7–12]. Among them, adsorptive corrosion inhibitor, namely self-assembled monolayers (SAMs) inhibitor [13–18], can effectively protect copper from corrosion by forming compact

layers on copper surface. This method has many advantages, such as fast film-forming and high efficiency. Some organics such as alkylthiol [19], sulfone, phenylamine, aldehyde and some heterocyclic compounds containing S, N, P atoms have been developed as adsorptive corrosion inhibitors [20–25]. Laibinis et al. firstly reported the good performance of alkylthiol for copper protection under atmosphere condition [26]. Petrović et al. also demonstrated the protective ability of alkylthiol SAMs for copper in a sodium acetate solution [27]. Meanwhile, Wang et al. studied carbazole and N-vinylcarbazole adsorption films for protecting copper in a NaCl solution [28]. On the other hand, benzotriazole (BTA), a representative heterocyclic compound, possesses outstanding corrosion inhibition for copper, because it can not only inhibit the corrosion of copper, but also stabilize the copper ion in the media to prevent its deposition on copper [29]. Recently, Qin et al. reported effective protection for fresh copper by 2,5-Dimercapto-1,3,4-thiadiazole (DMTD) SAMs [30]. Further, Chen et al. found that 5-Mercapto-3-phenyl-1,3,4-thiadiazole-2-thione potassium (MPTT) could be adsorbed on copper surface and formed a hydrophobic film to protect the substrate [31]. Liao et al. reported that ammonium pyrrolidine dithiocarbamate SAMs could be formed on copper surface to achieve a good corrosion inhibition performance [32]. Previous studies demonstrated that the corrosion inhibition ability is enhanced when heterocycle and sulfhydryl groups coexist in a molecule due to the synergistic effect on

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corrosion inhibition. Therefore, most of current studies focus on using single compound containing both heterocycle and sulfhydryl groups for copper corrosion protection. However, on one hand, those compounds containing both heterocycle and sulfhydryl groups normally involve in complex synthesis and high cost, on the other hand, organic solvents are needed to dissolve the compounds for the self-assembling process, which leads to higher cost and is more toxic to environment than using aqueous media. To the best of our knowledge, there are few reports investigating on using separate heterocycle and sulfhydryl compounds to form binary SAMs on copper for protecting it from corrosion.

In this work, we choose octadecanethiol ($C_{18}H_{37}-SH$) containing sulfhydryl group and benzotriazole (BTA) containing heterocycle group to form binary SAMs to protect copper from corrosion. Aqueous media are used for the self-assembling process to avoid usage of organic solvents. The results show that the binary SAMs are superior to the single SAMs based on $C_{18}H_{37}-SH$ or BTA for corrosion protection of copper due to the synergistic effect between sulfhydryl and heterocyclic compounds.

2. Experimental

2.1. Chemicals

All the chemicals are analytical grade and purchased from Adamas Reagent Co. Ltd and Alfa Aesar Co. Ltd. Deionized water was used as the solvent of all the aqueous solutions.

2.2. Preparation of the working solutions

The formula of various working solutions (A: $C_{18}H_{37}-SH$ working solution, B: BTA working solution, C: $C_{18}H_{37}-SH$ &BTA working solution) are listed in Table 1. A surfactant was added to assist the dispersion of $C_{18}H_{37}-SH$ due to the limited solubility of $C_{18}H_{37}-SH$ in water.

2.3. Preparation of the specimens

Firstly, copper (99.9%) sheets were ultrasonically washed in deionized water for three minutes to clean the surface. Then the specimens were immersed in a mixed alkali ($NaOH$ 60 g L⁻¹, Na_2CO_3 30 g L⁻¹, Na_3PO_4 20 g L⁻¹) solution at 65 °C for 3~5 minutes to remove the oil stains on the surface. The specimens were then dipped in a polishing solution (H_3PO_4 540 mL L⁻¹, CH_3COOH 300 mL L⁻¹, HNO_3 100 mL L⁻¹) at 85 °C for ~30 seconds. Lastly, the specimens were activated in a dilute sulfuric acid solution, then thoroughly rinsed in deionized water and dried in a stream of cold air.

The SAMs was obtained by dipping copper specimens into the working solutions at 25 °C for approximately five minutes. The BTA/ $C_{18}H_{37}-SH$ SAMs were acquired by dipping copper in working solution B firstly, and then in working solution A. The $C_{18}H_{37}-SH$ /BTA SAMs were obtained by dipping copper in working solution A first and then in working solution B. The $C_{18}H_{37}-SH$ &BTA SAMs were obtained by dipping copper into working solution C. The BTA SAMs and $C_{18}H_{37}-SH$ SAMs were obtained by immersing the copper specimens in B and A working solutions, respectively.

Table 1
The formula of various working solution.

	$C_{18}H_{37}-SH/g L^{-1}$	BTA/g L ⁻¹
A: $C_{18}H_{37}-SH$ working solution	2	/
B: BTA working solution	/	2
C: $C_{18}H_{37}-SH$ &BTA working solution	2	2

2.4. Structure and composition characterization of the SAMs

Surface-enhanced Raman spectroscopy (SERS), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were employed to characterize the structure and composition of the SAMs formed on copper specimens. FTIR spectrometer was in reflection mode with a spectral resolution of 2 cm⁻¹, and the angle between the horizontally polarized incident light and the normal direction of specimen was 80°. Raman measurement was performed by using the laser confocal micro-Raman spectrometer system RamLab-010 (Jobin Yvon) with a He-Ne Lasers beam of 632 nm operated at 5 mW and exposing time of 20 s. XPS analysis was conducted on an ESCALAB250 XPS spectrometer with an Mg Ka X-ray source (1350 eV).

2.5. Electrochemical performance of the SAMs

Electrochemical measurements were performed in a 3.5 wt% NaCl solution with a three-electrode system, which consisted of an exposed working electrode of 1 cm², a saturated calomel reference electrode (SCE) and a platinum counter electrode, on an electrochemical workstation (Model: CHI 660C). The tip of the reference electrode was positioned at a very close proximity to the working electrode surface in order to minimize ohmic potential drop. The electrochemical impedance spectroscopy (EIS) measurement was carried out at the open circuit potential over a frequency range from 0.01 Hz to 100 kHz with a sinusoidal potential perturbation of 5 mV in amplitude. The impedance data were analyzed with the ZSimpWin software. All the potential values in this paper are relative to SCE. The polarization curves were obtained independently for the anodic and cathodic curves from the corrosion potential with a scan rate of 1 mV·s⁻¹ (a minimum of six separate scans was performed to avoid occasionality).

3. Results and discussion

3.1. Structure and composition of the various SAMs

The chemical structure of the various SAMs on copper was investigated by SERS and FTIR. Fig. 1 shows the SERS spectra of three SAMs on copper substrate, and Table S1 summarizes the SERS data. Four main peaks located at 632/782 cm⁻¹, 1391 cm⁻¹ and 1596 cm⁻¹ are observed in BTA SAMs (Fig. 1), which are assigned to the triazole ring vibrating, triazole ring and benzene stretching

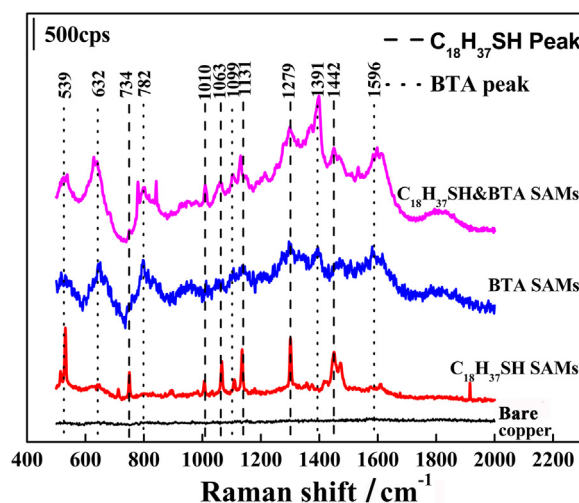


Fig. 1. SERS spectra of the $C_{18}H_{37}-SH$ &BTA SAMs, $C_{18}H_{37}-SH$ SAMs and BTA SAMs on copper surface.

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