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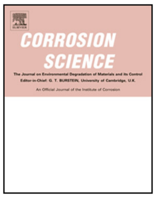

# The polymeric nanofilm of triazinedithiolsilane fabricated by self-assembled technique on copper surface. Part 1: Design route and corrosion resistance

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ABSTRACT

A novel design route for metal protection against corrosion is proposed for the first time, which lies in assembling two or more categories of protective groups to produce brand-new compounds and fabricating the corresponding resistance structure by means of various techniques. A kind of triazinedithiolsilane compound has been successfully synthesized as protector for copper by combining protective triazinedithiol and silane groups. The protective capability of the polymeric nanofilm prepared by heating the self-assembled monolayer (SAM) of the synthesized triazinedithiolsilane molecule was examined by electrochemical tests. The results show that the polymeric nanofilm significantly inhibits copper corrosion.

## 1. Introduction

Copper (Cu), widely used in micro-electronics and chemical industries owing to excellent electrical and thermal conductivities, is an active metal that cannot resist corrosion [1]. Enormous corrosion inhibitors, nanofilms and coatings have been accordingly explored with different fabrication techniques for copper protection. One of the most effective approaches is to prepare self-assembled monolayer (SAM) of organic inhibitors on copper surface [2]. Thus, a series of organic inhibitive compounds have been investigated, such as benzotriazole [3], thiol, dithiol and dithiocarboxylic [4], silane [5], triazinedithiol [6]. Considering that each category of organic inhibitors possesses limited functional groups which react with copper surface and resist corrosion limitedly, many scientists mainly concentrated on synthesizing inhibitors' derivatives with more reactive sites to generate a highly packed ad-layer/SAM as corrosion resistance [7,8], developing mixed self-assembled monolayers [9] or constructing composite nanofilms by diverse methods [10].

However, no investigation has been attempted to assemble two or more categories of protective groups in various compounds to produce brand-new compounds, reveal their protection capabilities, and elucidate the protective mechanisms. Most studies only concentrate on changing organic functional groups of the main molecules, such as p-(9-(2-Methylisoxazolidin-5-yl)nonyloxy)benzaldehyde and its derivates [11], thiophene schiff base [12], and di-quaternary ammonium salts [13]. In this study, by following the above idea shown in Fig. 1, we propose a novel design route and have synthesized a new molecule through assembling protective triazinedithiol (TDT) groups and silane groups into one compound. This kind of compound is defined as triazinedithiolsilane. 6-(3-triethoxysilylpropyl)amino-1,3,5-triazine-2,4-dithiol monosodium salt (TESPA-TDT, abbreviated as TESPA in Fig. 1) is one of such target molecules we have prefabricated. Triazinedithiol and its monosodium salt, without unfavorable mercaptan smell and toxicity as environmentally friendly compounds due to a tautomer of thiol-thione type [14], could be self-assembled on copper surface via chemical bonds between copper atoms and thiol/dithiol groups (—SH). The obtained SAM could polymerize at high temperature, developing a polymeric nanofilm of disulfide (the left red structure in Fig. 1) [15]. Silane could produce siloxane network (SiOSi) with silanol groups (SiOH) initially formed by the hydrolysis of $SiOC_2H_5$ groups through releasing water in a curing process (the top blue cross-linking texture in Fig. 1) [16]. The designed TESPA theoretically provides two kinds of protective structures, however, originated from one kind of compound to resist copper corrosion.

Our work is devoted to synthesizing the designed TESPA molecule according to the route, preparing its nanofilms based on

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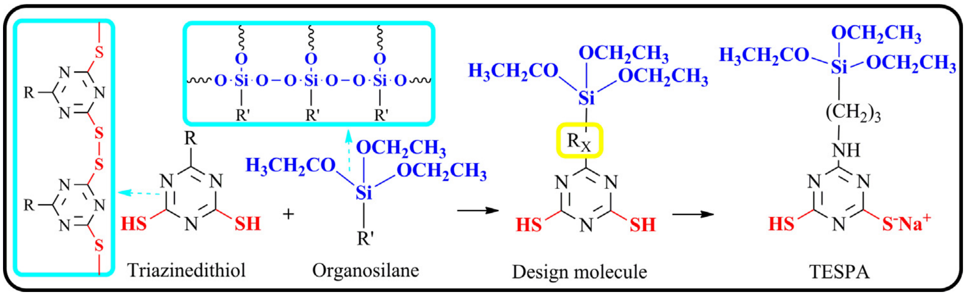

**Fig. 1.** A representative (TESPA) of the design route proposed in this study. Triazinedithiol can react with copper and form protective —SS— structure upon heating; organosilane can hydrolyze and develop protective SiOSi network when heated. Rx of the design molecule represents different functional groups which can be altered.

triazinedithiol chemistry and silane chemistry, understanding protection performance of the two functional groups, and revealing the protective structure of TESPA on copper by utilizing a variety of electrochemical tests and contact angle measurement.

## 2. Experimental

### 2.1. Synthesizing One of the Triazinedithiolsilane Molecules

6-(3-triethoxysilylpropyl)amino-1,3,5-triazine-2,4-dithiol monosodium salt was synthesized by reacting 6-(3-triethoxysilylpropylamino)-1,3,5-triazine-2,4-dichloride with NaSH [17]. The chemical structure of TESPA was identified by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR), and mass spectroscopy (MS) (The data are available in Supplementary Data). 1H NMR and 13C NMR spectra were recorded by Bruker AC 400 with 500 MHz (Bruker Daltonics, Billerica, MA, USA). FT-IR spectra were measured using Bruker TENSOR 37 (Bruker Daltonics). MS was recorded by LCQFleet (Thermo Scientific, Waltham, MA, USA).

### 2.2. Preparation of the Polymeric Nanofilm of TESPA

The TESPA self-assembly solution consists of 5 mM TESPA monomer dissolved in ethanol/distilled water (95/5, (v/v)) mixed solvent, with pH of 5 by adding acetic acid examined by means of pH meter. The solution was stirred adequately and hydrolyzed for different time at 35 °C. Millipore-Q water (18.2 MΩ cm) was used in all solutions. Unless noted otherwise, all reagents used were of analytical grade. Conductivity measurements were performed with a S470 Seven-Excellence conductivity meter (Mettler-Toledo, Switzerland) equipped with a conductivity sensor. The pure copper plates, cut into the dimensions of 20 by 20 mm and 1 mm thick for electrochemical examinations, were abraded with emery paper of 800 grit and 1000 grit, and followed by fine polishing with alumina paste of 0.35, 0.2, 0.1 mm particle size to achieve a mirror finish. The samples then degreased with acetone and alcohol in an ultrasonic bath for 15 min, and finally rinsed with copious Millipore-Q water. After cleaning, the copper specimens were immediately immersed in TESPA solution for 15 min and dried by cold air from a hair dryer, aged at 100 °C for 15 min in an air oven. Herein, a bare copper and another one heated at 100 °C for 15 min were used as reference samples. To illustrate the protective abilities of TESPA on copper surface, a TESPA-treated sample and a TESPA treated one with heating at 100 °C for 15 min were investigated, respectively. The abbreviations of the four samples are as follows: Cu-Bare, Cu-Heat, Cu-TESPA, and Cu-TESPA-Heat. The purpose of Cu-Heat was to monitor the inhibitory action of copper oxide film produced both in Cu-Heat and Cu-TESPA-Heat situations when copper is thermally cured.

### 2.3. Electrochemical Measurements and Contact Angle

Electrochemical measurements were conducted on a PARSTAT 2273 workstation (Princeton Applied Research, USA) in a standard three-electrode system at 25 ± 1 °C. A solution of 3.5 wt% NaCl used as electrolyte was not deoxygenated and open to the air during each test process. The obtained four specimens were successively adopted as the working electrode with an exposed area of 1 $\text{cm}^2$ to the NaCl solution. A saturated calomel electrode (SCE) with a salt bridge in a Luggin capillary serves as the reference electrode and a platinum panel (2 $\text{cm}^2$) as the counter electrode. All potential values were referred to $E_{\text{SCE}}$. Cyclic voltammetry (CV) was performed through scanning the potential from −0.7– 0.6 V with a sweep rate 10 mV/s. Electrochemical Impedance Spectroscopy (EIS) was carried out in the frequency range from 100 kHz to 10 mHz with 12 points per decade at a 10 mV amplitude of the excitation signal under the open circuit potential (OCP, $E_{\text{OCP}}$ vs. SCE). All EIS data were collected after immersing the working electrodes in the electrolyte for 50 min to reach a stable situation. The resultant plots of $E_{\text{ocp}}$ vs. time for different surfaces are also given. The potentiodynamic polarization curves (Tafel) were recorded from ($E_{\text{ocp}}$ vs. SCE) – 350 mV to ($E_{\text{ocp}}$ vs. SCE) + 350 mV at a scan rate of 1 mV/s. Before the data were recorded, the tested coupons were also immersed in the electrolyte for 50 min in an attempt to achieve a steady state. Contact angle measurements were performed on a contact angle analyzer, XG-CAMB manufactured by Xuanyichuangxi Industrial Equipment Co., Ltd. (China, Shanghai). The data were collected at five different points on each sample surface resulting in an average value.

### 2.4. X-ray Photoelectron Spectroscopy (XPS)

XPS experiments were carried out on an ESCALAB 250Xi (Thermo Fisher Scientific) with Al Ka radiation ($h\upsilon = 1486.6$ eV; analyzed area = 600 $\mu\text{m}^2$). Unless specified otherwise, the X-ray anode was run at 250 W and the high voltage was kept at 15.0 kV with a detection angle of 45°. The software of XPS Peak 4.1 was adopted to de-convolve the S2p peaks using the Shirley-type background. We kept a combination of 80% Gaussian-20% Lorentzian line shape [18], and maintained the FWHM of the various components in a given spectrum as close as possible [19].

## 3. Results and Discussion

### 3.1. TESPA as one Representative of Triazinedithiol Compounds

The results of NMR, FT-IR, and MS suggest that TESPA has been successfully synthesized (see Supplementary Data), which opens up the possibility of utilizing triazinedithiol compounds as inhibitors for copper protection. Plenty of studies have confirmed that the chain length of the molecule influences its directional

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