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Self-assembled 1-octadecyl-1H-1,2,4-triazole films on copper for corrosion protection

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ABSTRACT

A film of 1-octadecyl-1H-1,2,4-triazole (OTA) was formed on a fresh copper surface by self-assembly technique. The optimum concentration of OTA and immersion time for the formation of a protective OTA film have been established using electrochemical impedance spectroscopy (EIS). These are (i) 15 mM concentration of OTA in methanol and (ii) immersion period of 48 h. X-ray photoelectron spectroscopy (XPS), reflection absorption FTIR spectroscopy, atomic force microscopy (AFM), and contact angle measurements have been used to characterize the OTA film on copper surface. The efficiency of OTA film to protect copper from corrosion in aqueous NaCl environment has been investigated using EIS, potentiodynamic polarization studies, cyclic voltammetry and weight-loss studies. All these studies showed that the OTA film affords excellent protection against corrosion of copper.

1. Introduction

High electrical and thermal conductivities, low cost and easy fabrication of copper have made it an important alternative to gold and aluminium in microelectronic packaging [1]. The main applications are in copper lead frames, heat sinks, foils for flexible circuits, interconnection wires, etc. However, unlike aluminium oxide, copper oxide is not self protective. Therefore, copper readily undergoes oxidation forming Cu_2O initially, which further oxidizes to CuO. Oxidation of copper is considered a serious reliability problem in microelectronic packaging. Therefore, protection of copper against oxidation is very important in microelectronics packaging.

Self-assembled films are dense and ordered ultrathin layers formed spontaneously by chemisorption on metal surface. The films act as effective barriers to protect the metal from corrosion [2]. The chemisorbed molecules organize themselves through van der Waals forces between them. Rondelez et al. described that the process of formation of self-assembled monolayer (SAM) consists of two steps, namely a fast adsorption step followed by a slow rearrangement to minimize the defects in the film [3]. Self-assembled films of long chain organic molecules containing sulphur are known to protect copper from corrosion. Laibinis and Whitesides reported that alkanethiols adsorbed on copper surface form densely packed SAMs, which were found to be effective inhibitors of copper corrosion in air [4]. Feng et al. reported corrosion protection ability of self-assembled alkanethiol monolayer on copper in a 0.5 M NaCl solution [5]. Aramaki and co-workers reported that the maximum efficiency of octadecanethiol modified copper for protection of copper from corrosion in 0.5 M Na_2SO_4 solution was 80.3% [6]. Appa Rao et al. studied the corrosion protection ability of self-assembled 5-methoxy-2-(octadecylthio) benzimidazole and 2-(octadecylthio) benzothiazole on copper in aqueous NaCl solution [7,8].

A few studies on protection of copper by self-assembly of nitrogen containing organic molecules have also been reported in the literature. Wang et al. compared the protection efficiencies of two types of self-assembled films namely carbazole and N-vinyl carbazole on copper. Their protection efficiencies were reported as 91.1% and 93.4%, respectively [9]. Quan et al. studied the SAMs of Schiff bases namely N,N′-o-phenylen-bis(3-methoxy salicylidenimine)(V-o-Ph-V), N-2-hydroxy phenyl-(3-methoxy salicylidenimine) (V-bso) and N-octadecyl-(3-methoxy salicylidenimine)(V-odc) on copper surface in 0.5 M NaCl solution by using XPS, EIS and polarization studies. They reported that the films are formed by the interaction of copper with nitrogen in Schiff base molecules. The V-odc molecule has only one nitrogen as an electron pair donor to form a complex with Cu^+ ions on copper surface. It also has polar groups like —OH, $—OCH_3$ which reduce the hydrophobicity [10,11]. In the present study the OTA molecule is chosen for the following reasons. It has three nitrogen atoms as electron pair donors to form a more stable complex

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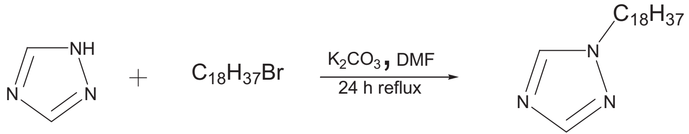
with Cu^+ ions on copper surface. It has a long alkyl chain and does not have any other polar groups and thus the film is likely to be more hydrophobic. Therefore, it was of interest to develop the optimum conditions for the formation of self-assembled films of 1-octadecyl-1H-1,2,4-triazole (OTA) on copper surface and to evaluate the corrosion protection ability of OTA film in aqueous NaCl environment. Moreover, the present study employed many experimental techniques, such as XPS, AFM, reflection absorption FTIR spectroscopy, contact angle measurements, EIS, potentiodynamic polarization studies, cyclic voltammetry and weight-loss studies, results of which provide a greater insight into the corrosion protection ability and mechanistic aspects of OTA film on copper surface.

2. Experimental

2.1. Synthesis of OTA

OTA was synthesized from equimolar amounts of 1-bromooctadecane and 1,2,4-triazole as per the procedure reported in the literature [12]. The reaction is given in Eq. (1). The structure of OTA is confirmed by IR and ^{1}H NMR spectra (not shown).



1H-1,2,4-triazole

1-octadecyl-1H-1,2,4-triazole (1)

2.2. Preparation of copper specimens

The working electrode was prepared from a copper sheet of purity 99.9%. For electrochemical impedance, potentiodynamic polarization and cyclic voltammetric studies, copper specimens of the dimensions 4.0 cm × 1.0 cm × 0.2 cm were used and only 1 cm^2 area was exposed to the electrolyte while the remaining area was insulated with the epoxy resin. For weight-loss studies also, the specimens of the dimensions 4.0 cm × 1.0 cm × 0.2 cm were used. For surface characterization studies, 1.0 cm × 1.0 cm × 0.2 cm specimens were used. The electrode surface was polished to obtain mirror finish using 1/0, 2/0, 3/0, 4/0 grade emery papers and alumina powder on a rotating disc and then degreased with acetone. The specimens were washed with double distilled water and dried with a flow of nitrogen gas.

2.3. Formation of self-assembled film on copper

Solubility of OTA molecule was tested in various organic solvents such as acetone, chloroform, ethyl acetate, ethanol, methanol and *n*-hexane. OTA was soluble only in methanol and hence methanol was chosen as the solvent. Exactly 1.2058 g of OTA was dissolved in 250 mL methanol to form a 15 mM solution, which corresponds to the solubility limit. Solutions of 5 and 10 mM were prepared by dilution from the 15 mM solution. The polished copper specimens were etched with 7N nitric acid for 30 s [9,10] to obtain a fresh and oxide free copper surface and then washed with double distilled water followed by the organic solvent and then immediately immersed in different concentrations of OTA solution in methanol for various immersion times (12–48 h) at room temperature. The specimens were then washed with methanol followed by double distilled water in order to remove loosely held molecules.

2.4. Electrochemical studies

Electrochemical studies were carried out in a three electrode cell assembly (in accordance with ASTM specifications) using an electrochemical work station model IM6e ZAHNER elektrik, Germany. The bare copper electrode or OTA modified copper electrode was used as the working electrode. A Pt electrode was used as the counter electrode and the reference electrode was Ag/AgCl/1 M KCl electrode.

The impedance studies were carried out at the open circuit potential in the frequency range from 60 kHz to 10 mHz with a sinusoidal potential perturbation of ±5 mV in amplitude. The impedance studies were first carried out to develop the optimum conditions for the formation of protective film on copper surface. These studies were also carried out in order to evaluate the corrosion protection ability of OTA film in an aggressive environment viz. aqueous NaCl solution at different concentrations (0.02–0.20 M) and at various immersion periods (1–24 h). Potentiodynamic polarization studies were performed in the potential range of −0.700 to +0.700 V vs. Ag/AgCl/1 M KCl at a scan rate of 2 mV/s. These studies were carried out at different concentrations (0.02–0.20 M) of aqueous NaCl environment. Cyclic voltammetric studies (CV) were carried out in 0.02 M NaCl in the potential range of −0.400 to +0.350 V vs. Ag/AgCl/1 M KCl at three different sweep rates of 30, 60 and 120 mV/s for two cycles at each sweep rate. The CV experiments were also carried out for 15 cycles at a constant sweep rate of 30 mV/s in the same potential range in order to study the stability of the OTA film.

2.5. Weight-loss studies

The bare copper specimens and the copper specimens covered with OTA film were immersed in 0.02 M NaCl solution for a period of 10 days. The weights of the specimens before and after immersion were recorded by using an electronic balance with a readability of 0.01 mg. From the weight-loss data, the corrosion rates and inhibition efficiencies were calculated. The studies were carried out in duplicate. The relative standard error in the corrosion rate determination is of the order of 2% or less [13].

2.6. Surface analytical studies

Reflection absorption FTIR spectra for bare copper and copper covered with OTA film were recorded in single reflection mode using FTIR spectrometer, Perkin Elmer Spectrum 100S in the spectral range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Bare copper and OTA film covered copper specimens were mounted on the reflection accessory and the plane polarized light was incident at a grazing angle of 80° from the surface normal. The sample compartment was continuously purged with nitrogen during the measurement. The contact angles on the bare copper and the OTA modified copper electrodes were measured by sessile water drop method using a contact angle measuring system, model G10, Kruss, Germany. Measurements were carried out under the ambient atmospheric conditions. XPS studies of the surface films were carried out using the X-ray photoelectron spectrometer, ESCA

Kratos model AXIS-165, with Mg Kα radiation (1253.6 eV) and sensitivity of 0.1 eV. Computer deconvolution was applied to identify the elemental peaks of copper, oxygen, nitrogen and carbon present in the film. Veeco Nanoscope IV multimode AFM was used to study the surface morphologies of bare copper and OTA modified copper. The AFM was used in contact mode between a silicon nitride tip attached to a micro cantilever and the surface of the sample.

3. Results and discussion

3.1. Optimum conditions for the formation of OTA film

Surface preparation of copper specimens by etching in 7 N HNO_3 for 30 s for formation of self assembled organic films on copper was established in the literature [9,10]. Such studies were always carried out at room temperature [10] as it is quite convenient. Therefore, in the present study also, surface preparation of copper specimens by etching in 7N HNO_3 for 30 s and room temperature of 30 °C were fixed. As already discussed under Section 2.3, OTA is soluble only in methanol. Therefore, methanol was chosen as the solvent. The optimum concentration of OTA and immersion period was established through impedance studies.

3.1.1. Effect of concentration of OTA

The best immersion time to obtain a dense and stable film was reported to be more than 20 h by Quan et al. in their studies on formation of a film of Schiff base on copper surface [10]. Our results showed that an immersion period of 48 h facilitates formation of an ordered film. Therefore, in the present study an immersion period of 48 h was first chosen and OTA films were formed on copper surface at various concentrations of OTA in the range of 5–15 mM. The impedance plots were recorded in aqueous 300 ppm chloride environment. Fig. 1A and B shows the Nyquist and Bode plots for the copper electrode covered with OTA film after immersion for 48 h in different concentrations of OTA at 30 °C. The phase angle vs. frequency plot reveals that with an increase in concentration of OTA from 5 to 15 mM the phase angle maximum is increased from 60° to 82° and it is more broadened. This result shows that at 15 mM concentration, the OTA film is close to capacitative behaviour. This plot shows two different phase angle maxima, indicating the model of two time constants. The impedance parameters are obtained using the equivalent circuit models shown in Fig. 2A and B. The circuit shown in Fig. 2A, with the Warburg element is used in the case of OTA film covered copper, where the Warburg impedance is seen. A constant phase element (*CPE*) was used as a substitute for the double layer capacitance in the equivalent circuits in order to fit the impedance data more accurately [14,15]. The *CPE* is a special element, whose value is a function of the angular frequency (w), and whose phase is independent of the frequency. Its admittance and impedance are, respectively, expressed as

$$Y_{CPE} = Y_0(jw)^{-n} \tag{2}$$

$$Z_{CPE} = \frac{1}{Y_0(jw)^{-n}} \tag{3}$$

where Y_0 is the magnitude of the *CPE*, j is the imaginary number ($j = (-1)^{1/2}$), w is the angular frequency, and n is the exponential term ($0 \leq n \leq 1$) of the *CPE*. n value indicates the roughness of the electrode. The lower the value of n, the rougher is the electrode surface. The lower value of n also relates to the inherent physical and chemical heterogeneous nature of the solid surface [16], the presence of a porous corrosion product layer [17] and the non-uniform distribution of current density on the surface. If $n = 1$, the impedance of a *CPE* is identical to the impedance of an ideal capacitor.

The charge transfer resistance (R_{ct}) and the film resistance (R_{film}) throw more light on the protective nature of the film. The parameters shown in Table 1 show that the R_{ct} and R_{film} values are increased enormously and the Warburg impedance in the Nyquist plots is disappeared in the case of film formed from 15 mM concentration of OTA. For example with increase in concentration from 5 to 15 mM, the R_{ct} value increased from 312.4 to 3187 kΩ cm^2, *CPE* values are decreased from 0.190 to 0.046 μF/cm^2 and the n value is increased from 0.80 to 0.93. Therefore, 15 mM concentration of OTA is chosen as the optimum concentration to form the film.

3.1.2. Effect of immersion period

By fixing the concentration of OTA as 15 mM, OTA films were formed on copper surface at different immersion periods in the range 12–48 h. Impedance studies were carried out in aqueous 300 ppm chloride environment and the corresponding Nyquist and Bode plots are shown in Fig. 3A and B. The corresponding impedance parameters are shown in Table 2. The results indicate that with an increase in immersion period R_{ct} value is increased to a very high value. For example with increase in immersion period from 12 to 48 h the R_{ct} value is increased from 379.8 to 3187 kΩ cm^2. However, the increase in R_{ct} value from 36 to 48 h is relatively less. It indicates that film formation is completed at an immersion period of 48 h.

From the above studies it is inferred that the optimum conditions for the formation of OTA films on copper surface are (i) 15 mM concentration of OTA in methanol and (ii) 48 h immersion period. These conditions were used for formation of OTA films on copper surface throughout the studies at a room temperature of 30 °C.

3.2. Characterization of OTA film

3.2.1. X-ray photo electron spectroscopic studies

In the XPS survey spectrum of bare copper, the peaks due to Cu 2p, C 1s and O 1s electrons are detected. The computer deconvolution spectra for copper, carbon and oxygen are shown in the Fig. 4(A–C), respectively. The Cu $2p_{3/2}$ peak at a binding energy of 932.6 eV and the Cu $2p_{1/2}$ peak at 952.4 eV can be attributed to Cu (I) [2]. The binding energy of C 1s electron at 285 eV corresponds to contaminant carbon, which is likely due to cracking of vacuum oil used in the XPS instrument [18]. The O 1s peak at 531.1 eV is due to formation of Cu_2O on the copper surface [19,20], which is formed during the interval between polishing of the copper surface and the XPS analysis.

The XPS survey spectrum of copper surface covered with OTA film shows peaks corresponding to Cu 2p, C 1s, O 1s and N 1s. The computer deconvolution spectra for copper, oxygen, carbon and nitrogen are shown in Fig. 5(A–D), respectively. Cu 2p spectrum shows peaks due to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ at 932.4 eV and 952.5 eV, respectively, which are due to the initial oxidation of copper surface to Cu_2O during film formation. Kamdem et al. reported in their studies that the Cu $2p_{3/2}$ peak at 935 eV and the presence of shake up satellites indicate the presence of cupric copper, while the peak around 933 eV and the absence of shake-up satellites indicate the presence of cuprous copper [21]. Therefore, it can be inferred that the peak observed in our studies at 932.4 eV without any shake-up satellites is due to the presence of cuprous copper in the OTA modified copper. The C 1s shows three peaks one each at 284.6, 285.8 and 287.2 eV. The intense peak at 284.6 eV is due to the presence of 18 carbon atoms in the alkyl chain of OTA film [22,23]. The C1s peak at 285.8 eV arises due to the contaminated carbon, which is likely due to cracking of vacuum oil used in the XPS instrument [18]. Another C1s peak at 287.2 eV corresponds to the carbons present in the triazole ring. The O1s spectrum shows a peak at 531.6 eV, which corresponds to oxygen of Cu_2O formed on copper surface. N 1s spectrum shows two peaks, which are due to the presence of nitrogen atoms in OTA molecule in different chemical environments. The peak at 399.6 eV is due to nitrogen in the second

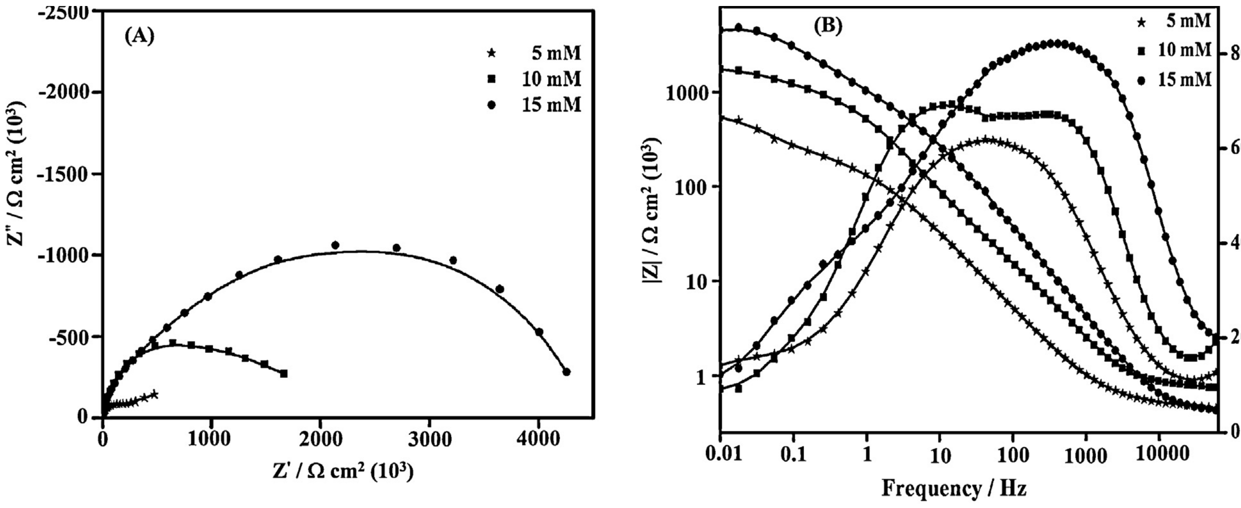


Fig. 1. (A) Nyquist and (B) Bode plots of copper covered with OTA film formed in different concentrations of OTA [environment: aqueous 300 ppm chloride, temperature: 30 °C].

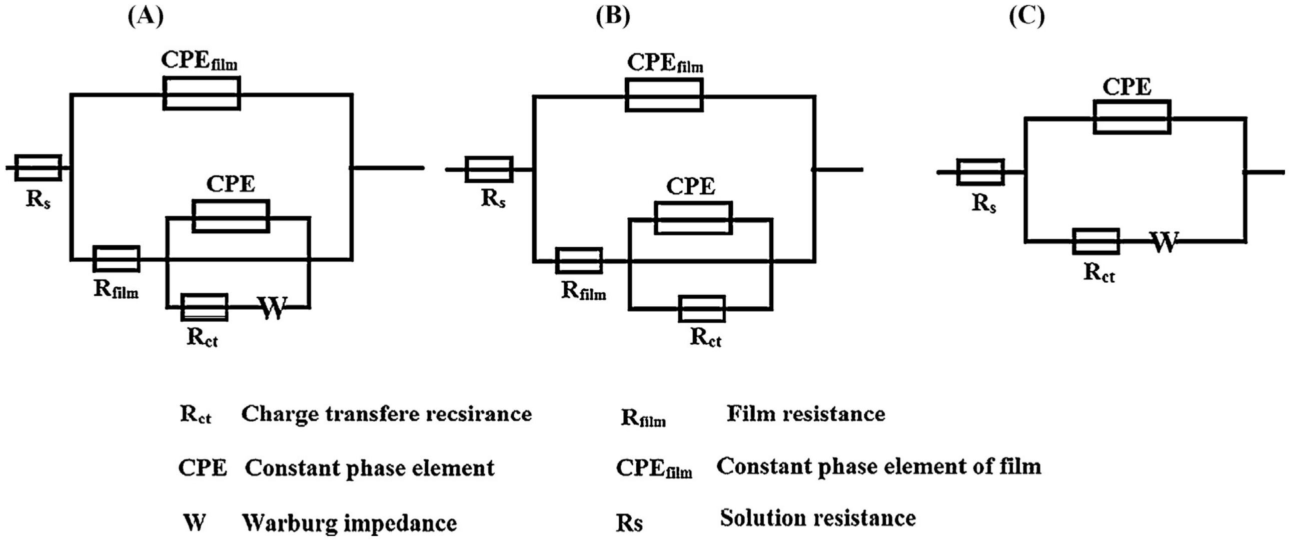


Fig. 2. Equivalent circuits used in impedance measurements of (A) copper covered with OTA film with Warburg, (B) copper covered with OTA film and (C) bare copper.

Table 1
Impedance parameters of copper covered with OTA film formed in different concentrations of OTA (environment: aqueous 300 ppm chloride, immersion period: 1 h, temperature: 30 °C).

S. No.	Concentration of OTA (mM)	R_{ct} (kΩ cm²)	CPE_{dl} (μF/cm²)	n	R_{film} (kΩ cm²)	CPE_{film} (μF/cm²)	n_{film}
1	5	312.4	0.190	0.80	228.7	0.900	0.71
2	10	1280	0.066	0.81	456.0	0.576	0.71
3	15	3187	0.046	0.93	621.9	0.046	0.74

Table 2
Impedance parameters of copper covered with OTA film formed at 15 mM OTA at different immersion periods (environment: aqueous 300 ppm chloride, immersion period: 1 h, Temperature: 30 °C).

S. No.	Immersion period for formation of OTA film (h)	R_{ct} (kΩ cm²)	CPE_{dl} (μF/cm²)	n	R_{film} (kΩ cm²)	CPE_{film} (μF/cm²)	n_{film}
1	12	379.8	0.093	0.75	187.2	0.089	0.62
2	24	665.8	0.054	0.86	335.7	0.023	0.67
3	36	2982	0.041	0.94	374.5	0.008	0.61
4	48	3187	0.046	0.93	621.9	0.046	0.71

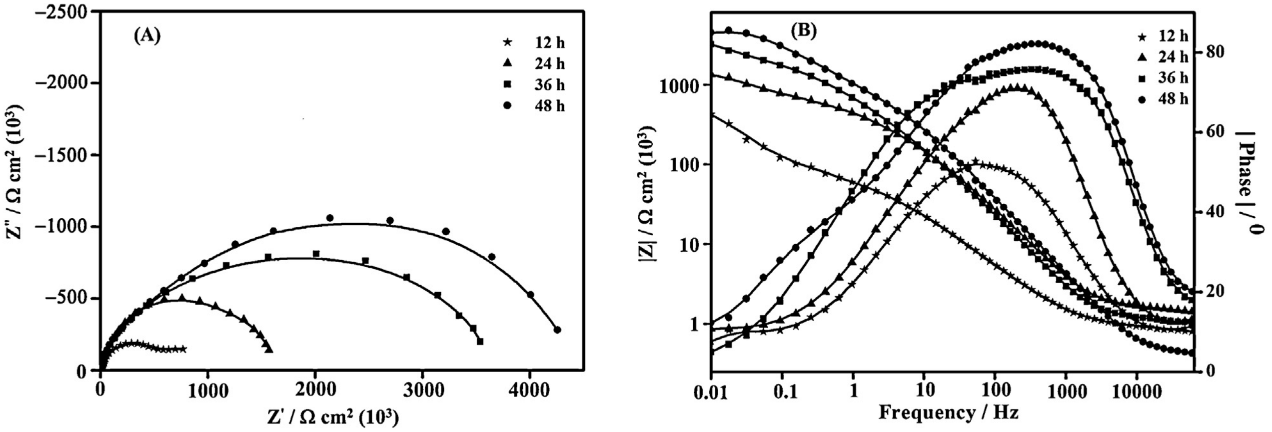


Fig. 3. (A) Nyquist and (B) Bode plots of copper covered with OTA film formed in 15 mM OTA at different immersion periods [environment: aqueous 300 ppm chloride, temperature: 30 °C].

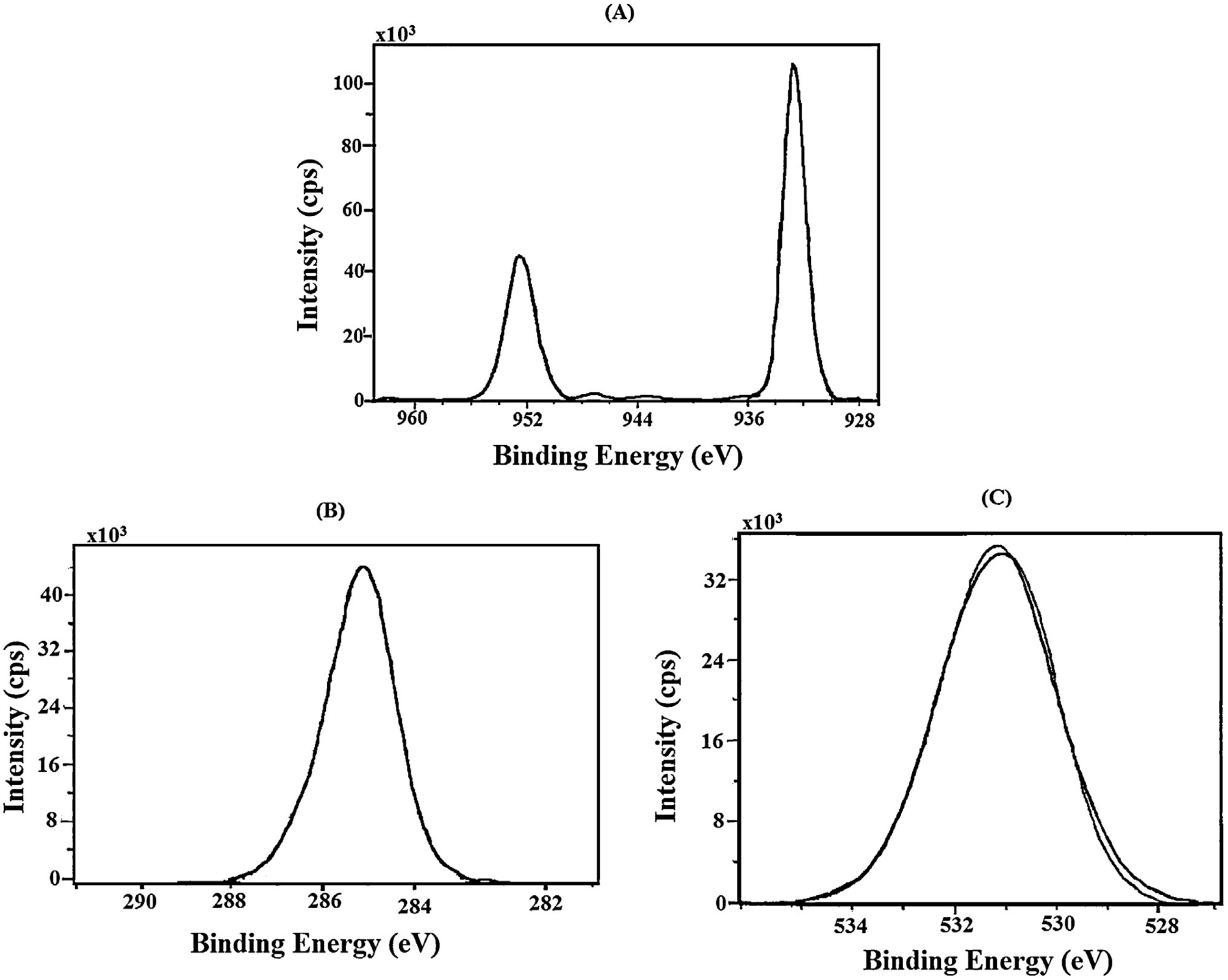


Fig. 4. XPS deconvolution spectra of different elements present on the surface of bare copper (A – Cu 2p, B – C 1s, C – O 1s).

and fourth positions and the other one at 401.6 eV is attributed to nitrogen in the first position of OTA molecule. The characteristic binding energy of the elemental nitrogen was reported at 398.0 eV in the literature [24]. The shift in elemental binding energies of N1s reveals that the nitrogen atoms present in OTA molecule are involved in the complex formation with cuprous ions [18].

3.2.2. Reflection absorption FTIR spectral studies

Reflection absorption FTIR spectra for bare copper and the copper coated with OTA film are shown in Fig. 6A and B, respectively. For bare copper, the spectrum shows a peak at 445 cm^{-1}, which is assigned to cuprous oxide on the surface [25]. This peak is absent in the spectrum of the OTA modified copper surface. On

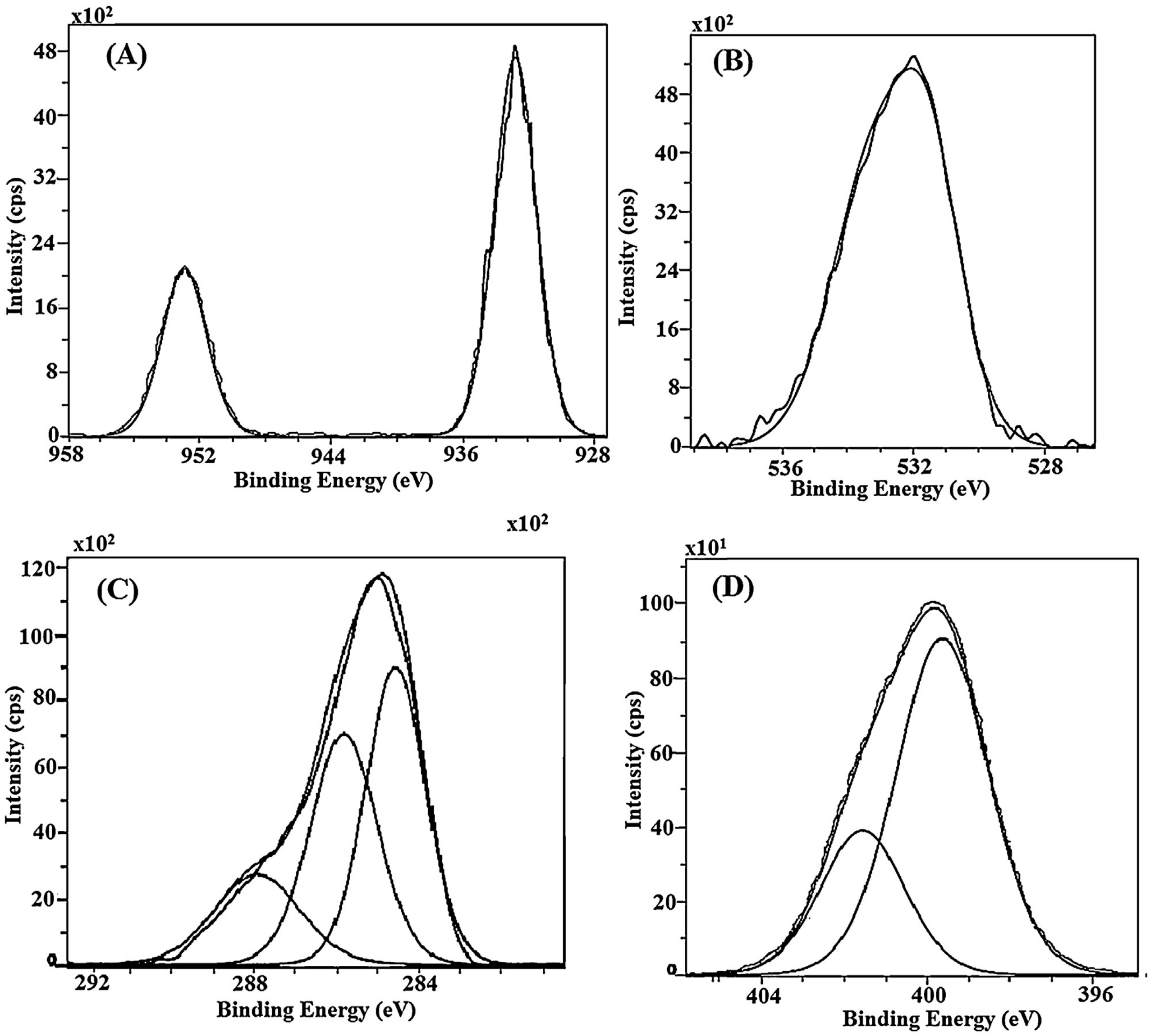


Fig. 5. XPS deconvolution spectra of different elements present on the surface of copper covered with OTA film (A – Cu 2p, B – O 1s, C – C 1s, D – N 1s).

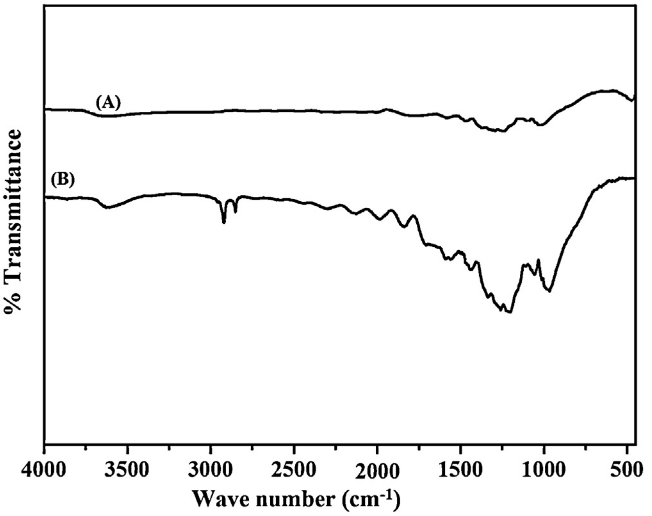


Fig. 6. Reflection absorption FTIR spectra of (A) bare copper and (B) OTA modified copper.

the other hand, the spectrum of OTA modified copper exhibits two bands, one at 2855 cm^{-1} and the other at 2928 cm^{-1}, which are due to CH_2 symmetric stretch and asymmetric stretch modes, respectively. Mekhalif et al. studied the comparative assessment of *n*-dodecanethiol and *n*-dodecaneselenol monolayers on electroplated copper. In their infrared reflection absorption study they interpreted the two bands at 2851 and 2922 cm^{-1} to the CH_2 symmetric stretch and asymmetric stretch modes, respectively [26]. Yoshida and Ishida studied FTIR reflection absorption spectrum of undecylimidazole on copper surface. They obtained two bands at 2853 and 2925 cm^{-1} and interpreted them to CH_2 symmetric stretching and asymmetric stretching modes, respectively [27]. Thus, there is a clear evidence of presence of aliphatic hydrocarbon chain in the film. The FTIR reflection absorption spectrum of OTA film covered copper also shows C=N stretching band at 1436 cm^{-1} and C—N stretching band at 1223 cm^{-1}. These peaks infer the formation of a film of OTA on the copper surface. The lowering of characteristic C=N stretching band from 1600 cm^{-1} [28] to 1436 cm^{-1} infers the formation of a complex between OTA and copper surface through nitrogen.

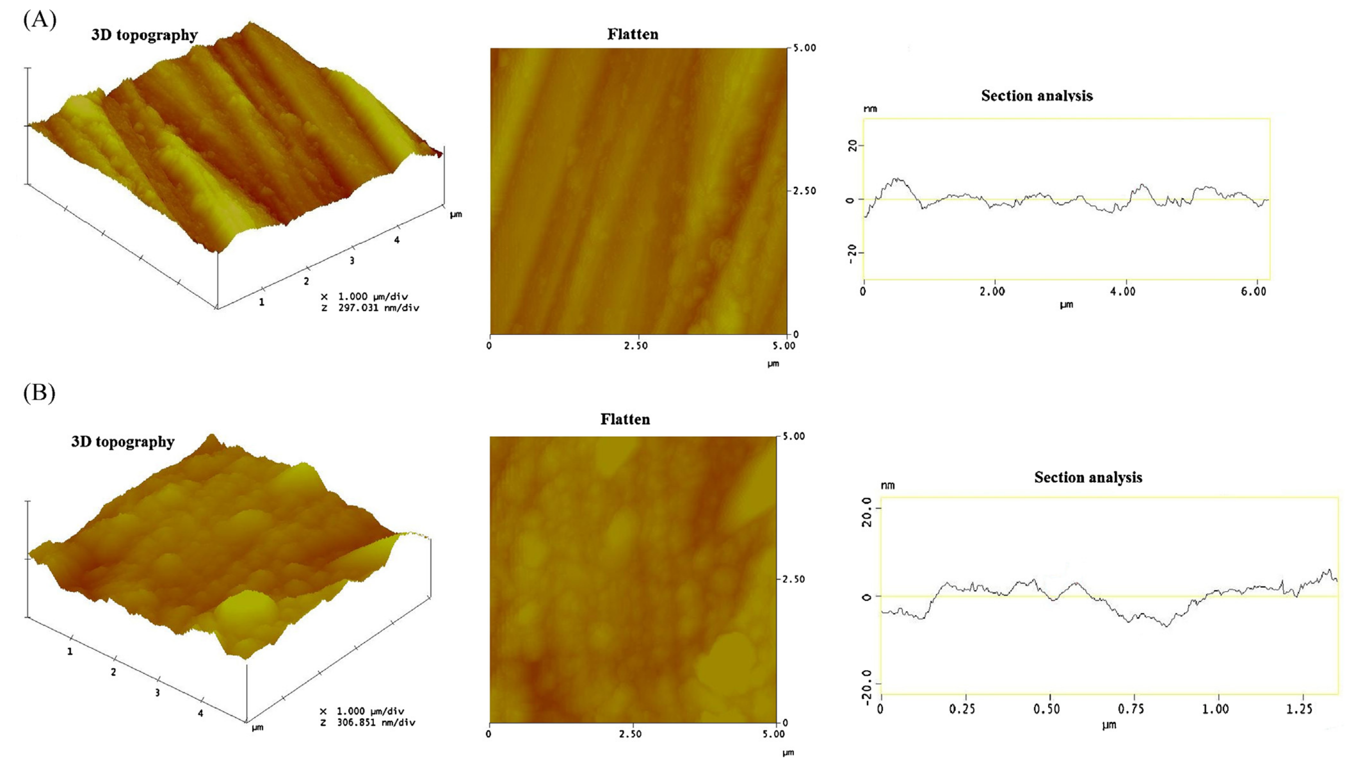


Fig. 7. AFM images of (A) bare copper and (B) OTA film covered copper.

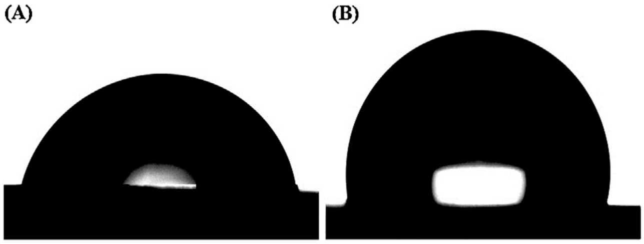


Fig. 8. Contact angle images of (A) bare copper and (B) OTA film covered copper.

3.2.3. *Atomic force microscopy*

The surface morphologies of polished copper and OTA modified copper are studied by AFM. Fig. 7A and B shows the AFM images namely 3D-Topography, flatten and section analysis of the polished and OTA film covered copper, respectively. The root mean square (rms) roughness measurements were carried out for both polished and OTA film protected copper. The vertical lines in the polished copper sample are due to the fine scratches obtained during the polishing process [29]. These polishing scratches result in rms roughness of 17.275 nm. The AFM image of copper surface covered with OTA film clearly shows that there is an ordered film of OTA formed and there is a reduction in the rms roughness to 14.174 nm. A uniform variation of the thickness in section analysis also indicates homogeneity of the OTA film.

3.2.4. *Contact angle measurements*

Fig. 8A and B shows the images of the sessile water drop on the bare and OTA modified copper surfaces, respectively. The contact angle values for bare copper and OTA modified copper are found to be 78° and 104°, respectively. Contact angle values are sensitive to the orientation of the molecules in the film. In well-ordered films, the terminal methyl group of the alkyl chain is oriented outward, reducing access of the water drop to the Cu surface. Higher contact angle value of OTA modified copper indicates an enormous improvement in the hydrophobicity when it is compared with oxidized Copper. The hydrophobicity of the OTA film is greater than that of the SAM formed by 4-aminobenzenthiol [30], 5-methoxy-2-(octadecylthio)benzimidazole [7] and 2-(octadecyl thiobenzothiazole) [8].

3.3. *Corrosion protection of copper by OTA film*

3.3.1. *Electrochemical impedance studies*

Impedance studies of bare copper and OTA modified copper electrodes were carried out in aqueous NaCl solution after 1 h equilibration, since the open circuit potential became stable within 1 h. Bode plots provided more valuable information than Nyquist plots. Hence only Bode plots are presented. Fig. 9A and B shows the Bode plots of bare copper and copper covered with OTA film, respectively, in NaCl solutions at different concentrations (0.02–0.20 M), at a constant immersion period of 1 h and at a constant temperature of 30 °C. The corresponding impedance parameters are shown in Table 3. EIS data of copper covered with film are best fitted by using the equivalent circuit shown in Fig. 2B, whereas for the bare copper in NaCl solution, the Bode plots are best fitted by using the equivalent circuit shown in Fig. 2C.

The Bode plots of phase angle and impedance vs. frequency show characteristic differences between the bare copper and copper covered with OTA film. In 0.02 M NaCl solution the Bode plot of bare copper exhibits a phase angle of 45°, whereas for the OTA film covered copper, the phase angle maximum is 84° and is shifted towards higher frequency side. R_{ct} value for bare copper in 0.02 M NaCl is 2.92 kΩ cm^2, which is increased to 2686 kΩ cm^2 for copper covered with OTA film in the same environment. The *CPE* value at the copper/0.02 M NaCl is decreased from 6.162 μF/cm^2 in the case of bare copper to a very small value of 0.003 μF/cm^2 in the case of copper covered with OTA film. The value of n is increased from 0.50 to

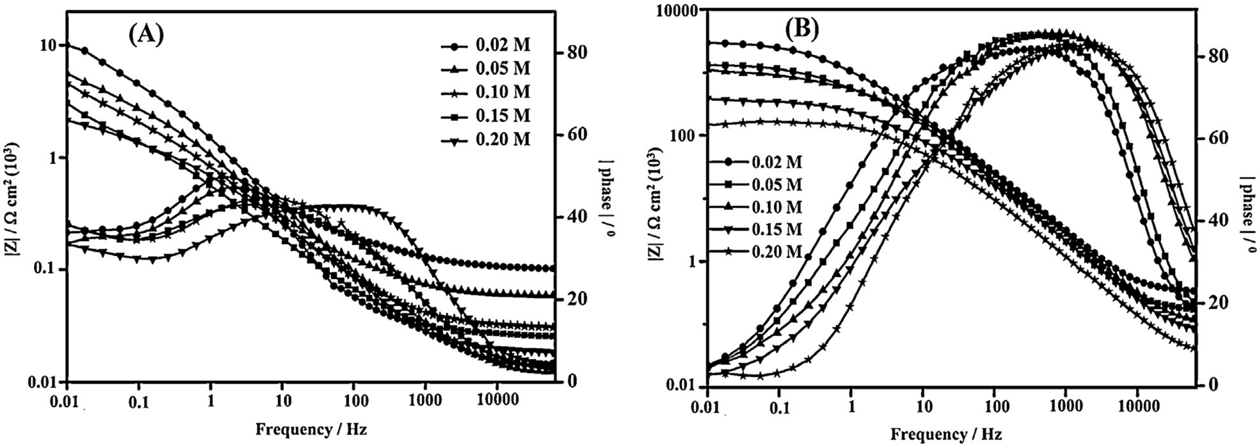


Fig. 9. Bode plots of (A) bare copper and (B) OTA film covered copper in different concentrations of NaCl [immersion period: 1 h, temperature: 30 °C].

Table 3
Impedance parameters of bare copper and copper covered with OTA film in aqueous NaCl environment at different concentrations (immersion period: 1 h, temperature: 30 °C).

S. No.	Specimen	Conc. (M)	R_{ct} (kΩ cm²)	CPE_{dl} (μF/cm²)	n	R_{film} (kΩ cm²)	CPE_{film} (μF/cm²)	n_{film}	IE (%)
1	Bare copper	0.02	2.920	6.162	0.50	–	–	–	–
2	Copper with OTA film	0.02	2686	0.003	0.92	490.7	0.050	0.54	99.9
3	Bare copper	0.05	2.781	7.966	0.47	–	–	–	–
4	Copper with OTA film	0.05	1232	0.008	0.96	239.1	0.074	0.52	99.8
5	Bare copper	0.10	2.685	9.101	0.47	–	–	–	–
6	Copper with OTA film	0.10	939.7	0.008	0.95	243.5	0.059	0.50	99.7
7	Bare copper	0.15	1.881	11.83	0.46	–	–	–	–
8	Copper with OTA film	0.15	369.8	0.017	0.95	29.25	0.073	0.56	99.5
9	Bare copper	0.20	1.152	12.15	0.42	–	–	–	–
10	Copper with OTA film	0.20	134.9	0.038	0.95	28.22	0.129	0.65	99.1

0.92 in the presence of OTA film. All these results indicate that the film is sufficiently densely packed to prevent diffusion of oxygen and other chloride ions on to the copper surface and thus protects copper from corrosion. Inhibition efficiencies are found to be in the range of 99.9–99.1% in NaCl environment within the concentration range studied.

The Bode plots of bare copper and copper covered with OTA film in 0.02 M NaCl solution at different immersion periods (1–24 h) at a constant temperature of 30 °C are shown in Fig. 10A and B, respectively. The corresponding impedance parameters are shown in Table 4. With increase in immersion period for OTA modified copper, there is a clear merger of the plots at the phase maxima. The decrease in R_{ct} values is very less. *CPE* and *n* values remain almost constant throughout the immersion period. These results reveal that the OTA film is highly homogeneous, non-porous and stable even after 24 h immersion time. The inhibition efficiencies are found to be 99.9% in 0.02 M NaCl environment at all the immersion periods.

3.3.2. *Potentiodynamic polarization studies*

Fig. 11A and B represents the potentiodynamic polarization curves of bare copper and OTA film covered copper, respectively. These studies were carried out in aqueous NaCl solution over a concentration range of 0.02–0.20 M after an immersion period of 1 h. The corrosion current densities (j_{corr}) are determined from the polarization curves by the Tafel extrapolation method. These values are shown in Table 5. Low j_{corr} values are obtained for copper covered with OTA film in comparison with the bare copper at all concentrations. The decrease in j_{corr} value is mainly due to the decrease of attack of chloride ions on the copper surface. With increase in NaCl concentration j_{corr} values are increased for both bare copper and OTA film covered copper. The cathodic current for the OTA film covered copper is much lower than the cathodic current of bare copper. These results infer that the OTA film effectively retards the cathodic reduction of oxygen and thus protects copper from corrosion. The anodic polarization curve of bare copper shows a current hump around 150 mV. This is due to the formation of CuCl which is an insoluble adsorbed species. With increasing the potential further towards anodic direction, current increases due to formation of Cu (II) species [31]. The OTA film covered copper shows a small current hump around 50 mV. It indicates less attack of chloride ions against copper in presence of OTA film. This result indicates the protective nature of OTA film on copper surface. The inhibition efficiency was calculated by using the equation

$$IE = \frac{j^0 corr - jcorr}{j^0 corr} \times 100 \qquad (4)$$

where $j^0{}_{corr}$ and j_{corr} are the corrosion current densities for the bare copper and OTA film covered copper electrodes, respectively. The inhibition efficiencies of the OTA film covered copper are in the range of 99.9–99.6% in aqueous NaCl environment within the concentration range studied. These results are in good agreement with those of impedance studies.

3.3.3. *Cyclic voltammetric studies*

Fig. 12A and B shows the cyclic voltammograms of bare copper and OTA film covered copper for 2 cycles at different sweep rates of 30, 60 and 120 mV/s. With an increase in the sweep rates from 30 to 120 mV/s, the anodic and cathodic peak currents of OTA film covered copper are slightly increased. Bare copper electrode exhibits two oxidation peaks at 0.150 and 0.350 V in forward scan and one large reduction peak at 0.160 V in the reverse scan. The

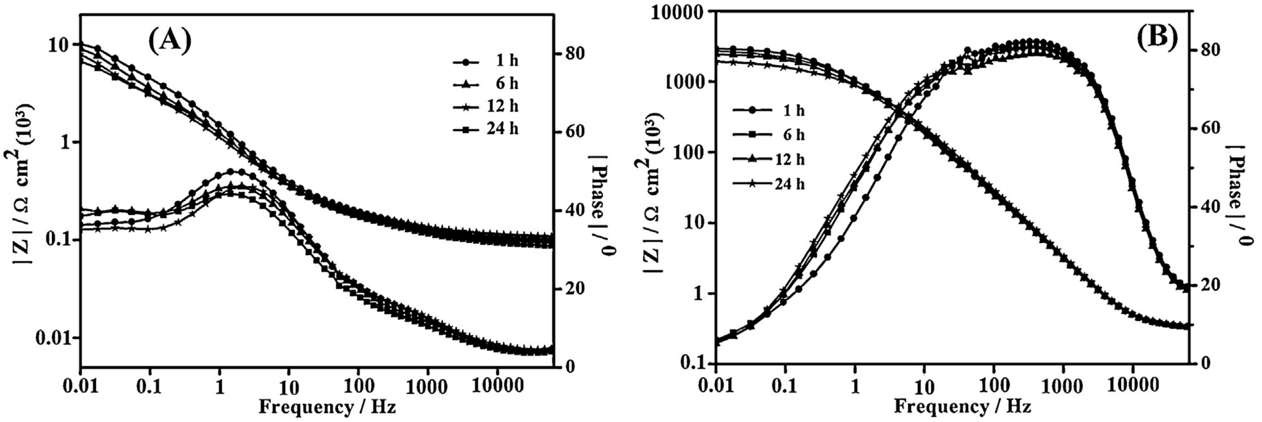


Fig. 10. Bode plots of (A) bare copper and (B) OTA film covered copper in 0.02 M NaCl at different immersion periods [temperature: 30 °C].

Table 4
Impedance parameters of bare copper and copper covered with OTA film in 0.02 M aqueous NaCl environment at different immersion periods (temperature: 30 °C).

S. No.	Specimen	Immersion time (h)	R_{ct} (kΩ cm^2)	CPE_{dl} (μF/cm^2)	n	R_{film} (kΩ cm^2)	CPE$_{film}$ (μF/cm^2)	n_{film}	IE (%)
1	Bare copper	1	2.920	6.162	0.50	–	–	–	–
2	Copper with OTA film	1	2686	0.003	0.93	490.7	0.050	0.54	99.9
3	Bare copper	6	2.785	6.263	0.49	–	–	–	–
4	Copper with OTA film	6	2411	0.003	0.93	578.5	0.049	0.50	99.9
5	Bare copper	12	2.518	6.338	0.48	–	–	–	–
6	Copper with OTA film	12	2179	0.004	0.91	510.6	0.051	0.50	99.9
7	Bare copper	24	2.435	6.569	0.46	–	–	–	–
8	Copper with OTA film	24	1764	0.004	0.93	460.4	0.047	0.46	99.9

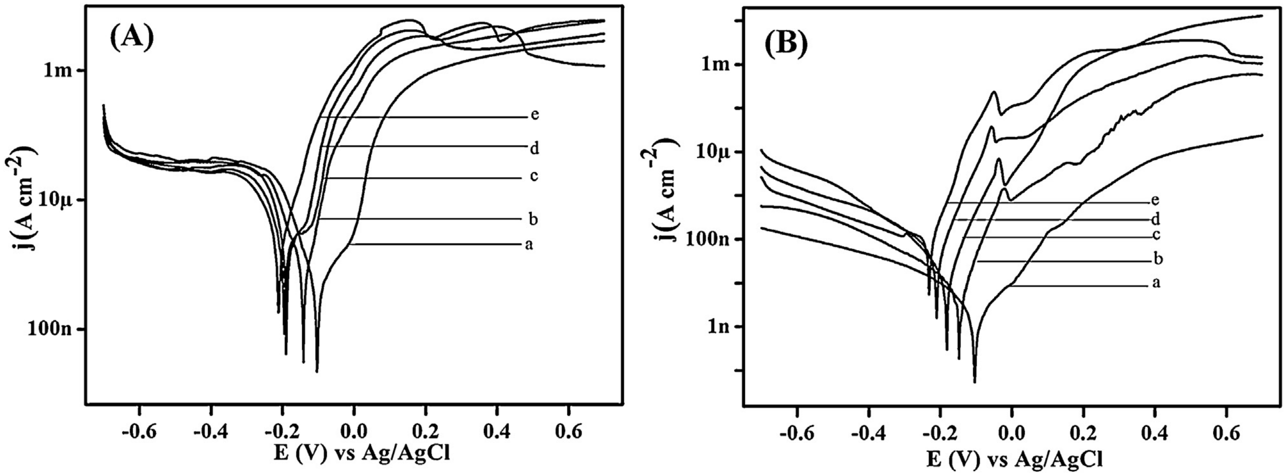


Fig. 11. Potentiodynamic polarization curves of (A) bare copper and (B) OTA film covered copper in different concentrations of NaCl. (a) 0.02 M, (b) 0.05 M, (c) 0.10 M, (d) 0.15 M and (e) 0.20 M [immersion period: 1 h, temperature: 30 °C].

Table 5
Corrosion parameters obtained by potentiodynamic polarization studies of bare copper and copper covered with OTA film in aqueous NaCl environment at different concentrations (immersion period: 1 h, temperature: 30 °C).

S. No.	Specimen	Concentration (M)	E_{corr} (mV)	j_{corr} (μA/cm^2)	b_a (mV/dec)	b_c (mV/dec)	IE (%)
1	Bare copper	0.02	−95.52	8.64	124	−305	–
2	Copper with OTA film	0.02	−101.5	0.001	31.5	−54.1	99.9
3	Bare copper	0.05	−147.9	11.8	116	−353	–
4	Copper with OTA film	0.05	−149.5	0.002	38.5	−40.5	99.9
5	Bare copper	0.10	−171.2	15.5	112	−393	–
6	Copper with OTA film	0.10	−177.4	0.010	41.4	−90.3	99.9
7	Bare copper	0.15	−198.2	15.8	121	−454	–
8	Copper with OTA film	0.15	−210.1	0.026	41.9	−88.7	99.8
9	Bare copper	0.20	−224.0	16.0	127	−406	–
10	Copper with OTA film	0.20	−232.3	0.068	51.1	−188	99.6

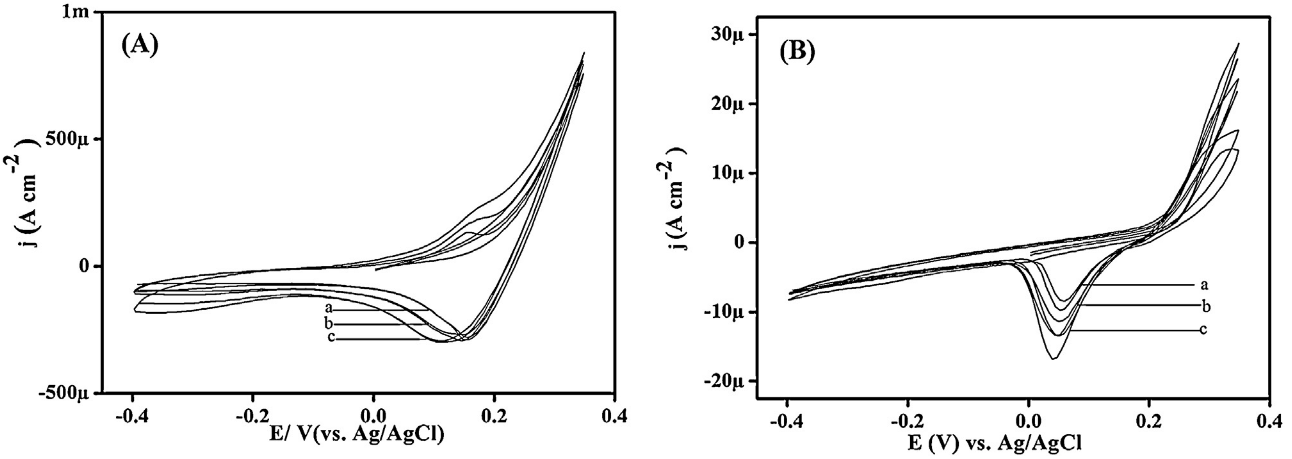


Fig. 12. Cyclic voltammograms in 0.02 M NaCl after 1 h immersion at different sweep rates (a – 30, b – 60, c – 120 mV/s): (A) bare copper and (B) OTA film covered copper.

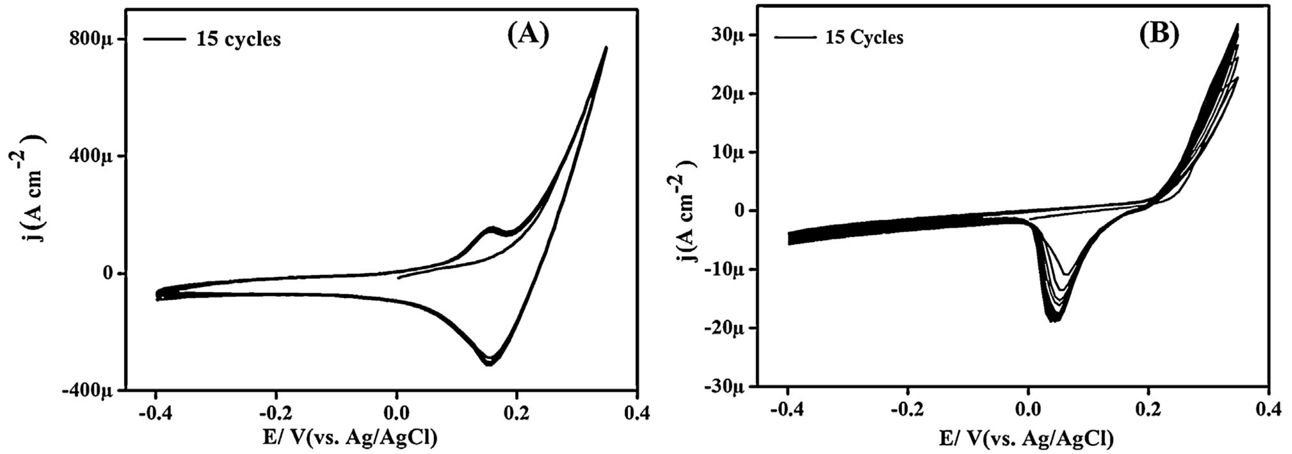


Fig. 13. Cyclic voltammograms in 0.02 M NaCl after 1 h immersion for 15 cycles at 30 mV/s: (A) bare copper and (B) OTA film covered copper.

first anodic peak corresponds to the formation of CuCl adsorbed layer as reported under 3.3.2, while the second peak is related to oxidation of Cu (I) to soluble $CuCl_2^-$ complex [9]. The large reduction peak corresponds to the reduction of soluble $CuCl_2^-$ complex and the CuCl layer formed on the copper surface to Cu. The OTA modified copper exhibits only one oxidation peak at 0.350 V in the forward scan and one reduction peak at 0.05 V in the reverse scan. Compared with bare copper, the cathodic and anodic peak currents of the OTA modified copper are far less and especially the oxidation from Cu (0) to Cu (I) was inhibited strongly after formation of OTA film on copper surface. For example, the anodic peak current decreased from 800 to 30 $\mu A/cm^2$ and the cathodic current decreased from 350 to 20 $\mu A/cm^2$ when the copper surface is modified with OTA film. Even when the number of cycles is increased to 15, the increase in both anodic and cathodic peak currents is not significant. Fig. 13A and B shows the cyclic voltammograms of bare copper and OTA film covered copper for 15 cycles at a constant sweep rate of 30 mV/s. This result infers the stability of the OTA film. Thus, CV studies also provide the evidence for the protection of copper surface from corrosion by OTA film in NaCl environment.

3.3.4. Weight-loss studies

Results of weight-loss studies for bare copper and OTA film covered copper after an immersion period of 10 days in 0.02 M aqueous

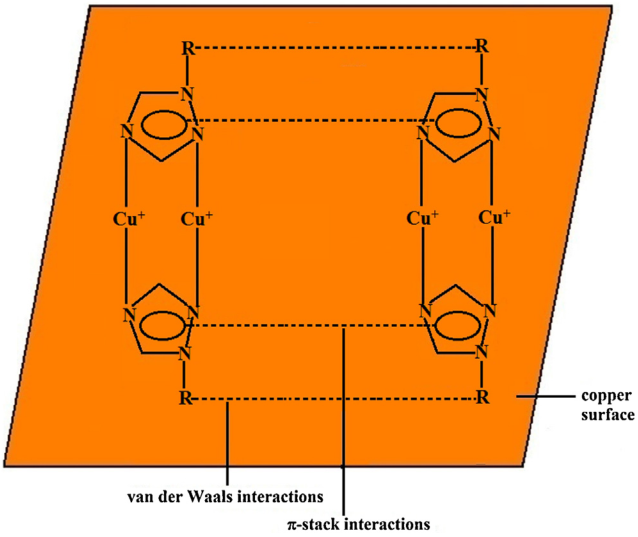


Fig. 14. Schematic illustration of formation of protective film by OTA on copper surface.

NaCl solution show corrosion rates of 0.0641 mmpy for former and of 0.0036 mmpy for the latter. These data result in an inhibition efficiency of 94.3%, which shows that OTA film protects copper quite effectively.

3.4. Mechanism of corrosion protection by OTA film

A plausible mechanism for corrosion protection of copper by OTA film is shown in Fig. 14. The higher values of contact angle indicate hydrophobicity of the film, which is possible when the OTA molecules are oriented nearly normal to the copper surface, with the head group on copper surface and long chain organic molecules pointing outwards. The OTA molecules get chemisorbed on the copper surface through nitrogen atoms and form a chelate with the Cu^+ ions available due to initial oxidation of copper. Cu^+ ions are known to form bidentate complexes with ligands. In addition to strong co-ordinate linkages between Cu^+ and N, there are non-covalent interactions namely van der Waals interactions between the long alkyl chains and π-stack interactions between the triazole rings, which result in the formation of a dense and defect free film on copper surface. Thus, there is formation of a [Cu^+–OTA] polymeric complex on copper surface, which is highly protective in nature.

4. Conclusions

The OTA self-assembled films on copper surface effectively protect copper from corrosion in NaCl solution within the concentration range and immersion period studied. AFM revealed the complete coverage of copper surface with OTA molecules. XPS and reflection absorption FTIR spectra inferred that the OTA molecules form chelated complexes with Cu (I) on copper surface. Contact angle measurements revealed the hydrophobic nature of OTA film. The inhibition efficiencies obtained from weight-loss studies, electrochemical impedance studies and polarization studies are in excellent agreement with each other. Polarization studies inferred that the OTA film functions as a cathodic inhibitor. Cyclic voltammetric studies showed that the OTA film is stable even after 15 cycles, when polarized to an anodic potential of 0.35 V vs. Ag/AgCl electrode.

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