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Deposition of Super-Hydrophobic Silver Film on Copper Substrate and Evaluation of Its Corrosion Properties

Fani Stergioudi ¹ , Aikaterini Baxevani ¹, Azarias Mavropoulos ¹ and Georgios Skordaris ^{2,*} 

¹ Physical Metallurgy Laboratory, Mechanical Engineering Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; fstergio@auth.gr (F.S.); ampaxeva@auth.gr (A.B.); azarias@auth.gr (A.M.)

² Laboratory for Machine Tools and Manufacturing Engineering, Mechanical Engineering Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

* Correspondence: skordaris@auth.gr

Abstract: A simple and versatile chemical solution deposition process is reported to manipulate the wettability properties of copper sheets. The whole process has the advantage of being time-saving low cost and environment-friendly. An adherent silver coating was achieved under optimal conditions. Scanning electron microscopy and X-ray diffraction were used to examine the silver film structure. A confocal microscope was used to record the 3D topography and assess the film roughness of the surface. A dual morphology was revealed, consisting of broad regions with feather-like structured morphologies and some areas with spherical morphologies. Such silver-coated copper samples exhibited a sufficiently stable coating with superhydrophobicity, having a maximum water contact angle of 152°, along with an oleophilic nature. The corrosion behavior of the produced hydrophobic copper under optimal conditions was evaluated by means of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) using a 3.5% NaCl solution. The corrosion protection mechanism was elucidated by the proposed equivalent circuits, indicating that the superhydrophobic silver coating acted as an effective barrier, separating the Cu substrate from the corrosive solution. The superhydrophobic coating demonstrated enhanced anti-corrosion properties against NaCl aqueous solution in relation to the copper substrate as indicated from both EIS and potentiodynamic polarization experiments.

Keywords: superhydrophobic; deposition process; corrosion properties; copper; equivalent circuit modeling



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1. Introduction

Superhydrophobic surfaces have attracted a lot of attention recently. They have potential uses as corrosion protection systems, in oil–water separation processes, as self-cleaning, anti-icing surfaces and as modified surfaces in bio-applications [1–6]. Different technologies have been utilized to generate rough micro- and nanostructures on metallic surfaces so as to provide superhydrophobicity and simultaneously improve their corrosion resistance [7–9].

The corrosion protection of copper remains an active research area, while numerous researchers attest that the deposition of superhydrophobic surfaces on copper substrates can act as an effective mean for corrosion protection [10–13]. Preparation of superhydrophobic copper surfaces has been reported in numerous papers by utilizing several techniques such as nanotextured surfaces by using laser beam machining [14] and nanocoatings by employing hydrothermal methods to fabricate CuO film on copper substrate [15]. Several chemical etching and hydrothermal methods, electrodeposition techniques and solution (wet) chemical reaction were also employed such as potentiostatic electrolysis in an ethanolic solution of tetradecanoic acid [16], oxidation in alkaline solutions [17], etching in ammonia solution combined with hydrothermal creation of copper oxide film [18], hydrothermal creation

of superhydrophobic Cu_2S film [19], electrolysis in capsaicin ethanolic solution [20], electrodeposition in myristic acid solution [21], chemical etching in an ammonia solution and consequent calcination in air [22], fabrication of multiscale textured surfaces on copper via electrodeposition in CuSO_4 and H_2SO_4 [23], an electrochemical modification process in an ethanolic stearic acid solution [24] and electrodeposition to develop multifunctional zinc/polydopamine composite hydrophobic coatings [25].

Nevertheless, most of the production techniques reported in literature suffer certain drawbacks, such as utilization of expensive raw material, long-lasting production stages that involve complicated processes under tight operating conditions or utilization of specific equipment. Consequently, finding a technique to generate a superhydrophobic surface on a copper substrate with a facile and versatile process, which is simultaneously cost effective, requires minimal instrument needs and employs more environmentally friendly procedures, is critical.

An important issue is the mechanical stability and corrosion protection of the hydrophobic coatings. Corrosion protection depends on mechanical stability and is one of the biggest problems facing scientists dealing with hydrophobic surfaces. So far, no hydrophobic coating has been found that meets the requirements for mechanical stability, high corrosion resistance and at the same time is produced by methods that do not require time-consuming stages and specialized equipment. This combination is a challenge and this will be the main scope of this paper.

In this research work, immersion in chemical solutions was used to effectively produce superhydrophobic silver coatings on copper sheet substrates. The procedure is divided into three stages: the growth of a silver film to improve micro roughness, immobilization of the silver film and functionalization with a polydopamine film, and finally, modification using thiol groups. Polydopamine (PDA) coating is broadly used for functionalization of surfaces via wet solution methods since it provides the creation of a functional and homogeneous coating on a wide range of substrates in an one-step reaction [26,27]. An additional advantage is that the polydopamine coatings are environmentally friendly since they are produced by simple self-polymerization of dopamine. Static water contact angle measurements were used to describe the wetting characteristics of the generated hydrophobic silver-coated copper. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to examine the silver film structure (XRD). A confocal microscope was used to record the 3D topography and assess the film roughness of the surface. The corrosion behavior of the produced hydrophobic copper under optimum conditions was evaluated by means of potentiodynamic polarization and electrochemical Impedance Spectroscopy (EIS) using a 3.5% NaCl solution. The production method proposed has the advantage of a simple, low cost and environment-friendly process and aspires to facilitate mass and industrial production of superhydrophobic copper.

2. Materials and Methods

2.1. Synthesis of the Hydrophobic Coating

The synthesis of the hydrophobic silver film on copper substrate was achieved via a four-stage process that involves immersion in solutions with a view to silver coat the copper surface. The final stage involved the modification of the silver coating to enhance the hydrophobicity. The stages followed for the production of the hydrophobic silver coating on copper sheets are schematically shown in Figure 1.

The copper sheets ($20 \times 20 \text{ mm}^2$) used as a substrates were initially cleaned mechanically by grinding using SiC paper with grit size 1200 grit size. Thereafter, the copper substrates were cleaned chemically in an ultrasonic bath for 15 min using acetone for removing any grease residues. Finally, they were immersed in 0.1 M HCl aqueous solution for 5 min and rinsed by water and ethanol.

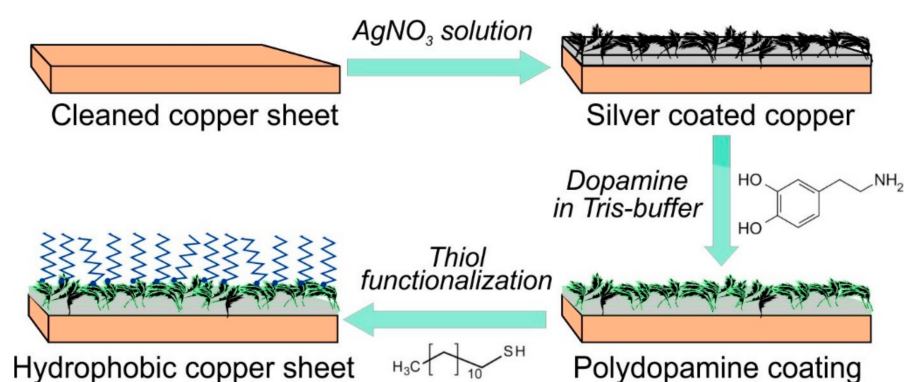


Figure 1. Schematic representation of the stages followed for the production of the hydrophobic silver coating on copper sheets.

The cleaned copper sheets were dipped in an aqueous solution of silver nitrate (AgNO_3) (4 mM) under different durations ranging from 5 to 50 min. The solution was continuously stirred (300 rpm) and the temperature was kept constant at 30 °C. The following step was the production of polydopamine coating which was achieved via the self-polymerization of dopamine as follows: 2 g/L dopamine (more specifically a dopamine derivative 3,4-dihydroxyphenylalanine (DOPA)), was introduced to a Tris-buffer solution at a temperature of 40 °C and constant stirring (300 rpm). The samples were then immersed for 20 min. For the preparation of the Tris-buffer solution 10 mM tris-hydroxymethyl-aminomethane ($\text{C}_4\text{H}_{11}\text{NO}_3$) was dissolved in distilled water acquiring a pH value of 10. The pH was adjusted from 10 to 7.5 with hydrochloric acid down to the desired value. The final step involved the reduction of surface energy which was accomplished by rinsing all specimens in an ethanolic solution of dodecanethiol (DDT) (0.1 M) for 1 h. All immersion stages for the coating process were carried out in a similar-sized beaker, allowing contact with air (oxygen) which is necessary for the self-polymerization of dopamine via oxidation.

2.2. Characterization of Modified Copper Surfaces

For smooth surfaces, static water contact angle (WCA) measurement can be used as an efficient tool to quantify the hydrophobicity. Therefore, static water contact angles were used to assess the wetting properties of the sample surfaces. Each measurement was taken using a 6 μL water droplet, to minimize the gravity impact and accurately determine the WCA.

Scanning electron microscopy (SEM, Bruker, Billerica, MA, USA) was used to evaluate the microstructure of the produced silver films. X-ray diffraction (XRD, 2-circle Rigaku Ultima+ X-ray diffractometer with radiation source of Cu ($\lambda_{\text{K}\alpha} = 0.15406 \text{ nm}$), Rigaku Corporation, Tokyo, Japan) was performed to determine the crystal structure of the produced hydrophobic coatings. The 3D topography and measurement of the surface's film roughness were captured using a confocal microscope (nanofocus μsurf , of NANOFOCUS AG, Oberhausen, Germany).

An ultrasonic procedure was employed to examine the silver coating adhesion and stability. The silver-coated copper sheets were immersed in distilled water and subjected to ultrasound at 25 °C for 60 min. The static water contact angles were measured at regular intervals to evaluate any loss of hydrophobicity provoked by this ultrasound treatment.

2.3. Corrosion Behavior of Silver-Coated Copper Surfaces

Potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS) tests were employed to investigate the corrosion properties of the silver-coated copper samples prepared under optimal conditions, thus exhibiting better hydrophobicity as indicated by the static contact angle measurements. As a reference material the corrosion properties of the copper substrate was used. All electrochemical experiments were performed in a three-electrode cell at room temperature (25 °C) using a 3.5% *w/v* NaCl aqueous solution. A

platinum plate and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The experimental installation of the electrochemical corrosion apparatus was in accordance with ASTM G69-20 [28] and ASTM G71-81 [29]. To ensure a steady state, the samples were immersed in the solution for at least 30 min at open circuit potential (OCP), before each polarization and EIS experiment. The polarization curves were obtained using a scan rate of 1 mV/s and a scan range from −600 to 800 mV (versus SCE) with respect to the OCP value. Corrosion density values were estimated and normalized to the surface area of each sample.

The EIS experiments were carried out at OCP (E_{OCP}) for a frequency range from 0.01 to 100 kHz using peak-to-peak voltage of 10 mV. A wide range of frequency was chosen so as to measure all possible corrosion and diffusion related phenomena taking place on the metal/solution interface. The EIS results were normalized to the surface area of each sample.

3. Results and Discussion

3.1. Influence of Various Parameters in the Synthesis Process of the Hydrophobic Coating

The process of producing the silver (Ag) coating is a crucial step that affects the hydrophobicity of the samples since different Ag film micro-morphologies are obtained. Therefore the deposition time in the $AgNO_3$ solution was investigated in this study. The role of the PDA coating is dual: to stabilize the uniform silver (Ag) coating and to serve as an anchor for the dodecanethiol ($CH_3(CH_2)_{11}SH$) hydrophobic molecule that forms a low-surface-energy self-assembled monolayer. More specifically, the thiol group adheres to the polydopamine coating, leaving the hydrophobic alkyl chain exposed to any solution. It is known that the process of dopamine-polymerization first involves oxidation of a catechol to a benzoquinone and that the formed PDA film comprises of free catechol groups available for further chemical surface modification [21,30,31].

The concentration of dopamine and the buffer were not varied. The “standard conditions”, as referred in literature [26,27,32], of 2 g/L dopamine in a Tris buffer, were used for producing surface functionalization of the copper samples. Preliminary experiments using higher concentrations of dopamine were conducted. However, the appearance of white aggregates on the surface of the polydopamine coatings which were visual by bare eye indicated a non-uniform coating process. These aggregates have been noticed in other studies also and were attributed either to un-oxidised dopamine or the presence of oxidized polydopamine in the solution, before reaching the surface of the sample [26–30]. Therefore, the concentration limit was set to 2 g/L.

The pH of the Tris buffer solution was considered a parameter worthy to examine since it is proven that it strongly affects the kinetics of the deposition of dopamine [30,33]. Therefore, the hydrophobicity of the films produced as a function of pH value of Tris buffer solution at a constant dopamine concentration was investigated.

The simultaneous coating of silver and PDA in one beaker was also investigated in order to minimize the stages of the coating production. However, for ad-layer formations (such is our case) the conventional two-step silver and PDA coatings to obtain immobilization of silver coating showed the most promising results. In the case of simultaneous deposition of silver and PDA coatings using one beaker the produced hydrophobic film was unsuccessful, having a contact angle of 140° , possibly due to the disturbance of PDA polymerization and the appearance of aggregations on the surface of the polydopamine coating. Moreover, it is known that the O- and N-sites of PDA can reduce the Ag^+ ions to Ag, promoting the formation of single Ag nanoparticles rather than the formation of leaf of dendritic Ag morphologies that are more useful in hydrophobic applications due to the micro-roughness increase that they offer [27].

3.2. Surface Morphology and Wettability of the Prepared Hydrophobic Coatings

Figure 2 depicts the WCA measurements for the produced silver-coated copper samples under different process conditions. Various hydrophobic ($WCA > 90^\circ$) and superhy-

drophobic ($WCA > 150^\circ$) copper surfaces were synthesized via immersion of the copper substrates in silver nitrate solution for durations of 5, 10, 15, 20, 30, 40 and 50 min. The pH effect of the Tris-buffer solution, used for the formation of the PDA coating, on the WCA is also illustrated in Figure 2. Three different pH values were examined. The initial contact angle received from the grinding process of the copper substrates was 128° . The direction of grinding did not influence the contact angle value for the copper samples.

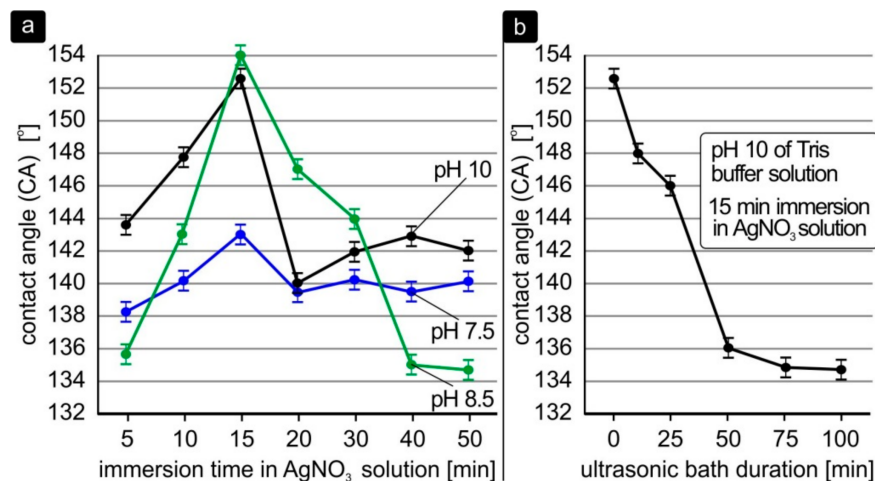


Figure 2. (a) Contact angle relative to the immersion time in silver nitrate solution and pH value of the Tris buffer solution, (b) contact angle after various durations in an ultrasonic bath for the optimum silver-coated superhydrophobic copper sample.

All the samples exhibited superhydrophobic behaviour for pH 8.5 of the Tris-buffer solution and immersion duration between 10 to 20 min. The water drop after its deposition on the surface showed an inability to hold on to the surface and rolled over the surface immediately. These silver-coated copper samples presented a uniform coating, having a black color, which leads to a superhydrophobic surface angle of 180° . However, these coatings were unstable. After a short period of contact with the environment these surfaces lost the optimal property to repel the water drop, while the WCAs of the droplets stabilized at the values that are depicted in Figure 2a.

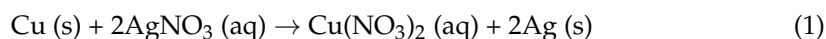
From Figure 2a it is clear that for all pH values of Tris buffer solution the WCA increases up to a maximum value, corresponding for all cases examined to 15 min immersion in silver nitrate solution. The slope of the curves is different indicating that different mechanisms and kinetics is probably taking place during PDA coating process at pH 7.5, 8.5 and 10 of the Tris-buffer solution. When the immersion time in silver nitrate solution is longer than 15 min the WCA decreases, irrespective of the pH of the Tris buffer solution until the value of $140\text{--}142^\circ$ for pH 7.5 and 10 of the Tris buffer solution and at the lower value of 134° for pH 8.5 of Tris buffer solution.

Overall, it was deduced that silver-coated copper samples exhibit superhydrophobic behavior with a maximum value of WCA at 154° and 152.5° when produced under 15 min immersion in the silver nitrate solution and pH 8.5 and 10 of the Tris buffer solution, respectively. Because the hydrophobic coatings produced using pH 8.5 of the Tris buffer solution were unstable, it was considered that the optimum value of pH for the Tris buffer solution was pH = 10. Correspondingly, the optimal immersion time in AgNO_3 solution was 15 min.

The initial evaluation of the adhesion and stability of the silver coating was performed by immersing the silver-coated samples in an ultrasonic bath for various durations and subsequently measuring the WCA. Possible abruption of the silver film was also investigated by visual inspection and optical microscopy. The hydrophobicity loss, as indicated by the WCA reduction, for the optimal silver-coated copper samples (15 min silver deposition, pH 10 of the Tris buffer solution) is shown in Figure 1. Although the WCA decreased after

50 min in the ultrasonic bath, it stabilized at a constant value of about 135° suggesting no further hydrophobicity loss. It is noteworthy that throughout the experiment no coating abrasion was observed even after 90 min in the ultrasonic bath, thus attesting that the stability and cohesion of the developed silver coatings on the copper substrate is sufficient.

The shape and morphology of the silver film obtained is considerably influenced by the immersion time in the nitrate silver solution. The silver salt is dissolved and the Ag cations are deposited via an electroless galvanic process (reaction (1)) to the copper substrate in order to produce a nano- or micro-roughened silver coating as follows [34]:



SEM images of the Ag coatings on copper substrate with different Ag deposition times are shown in Figure 3. The initial copper substrate used to develop the hydrophobic silver coatings is also presented, as a reference material.

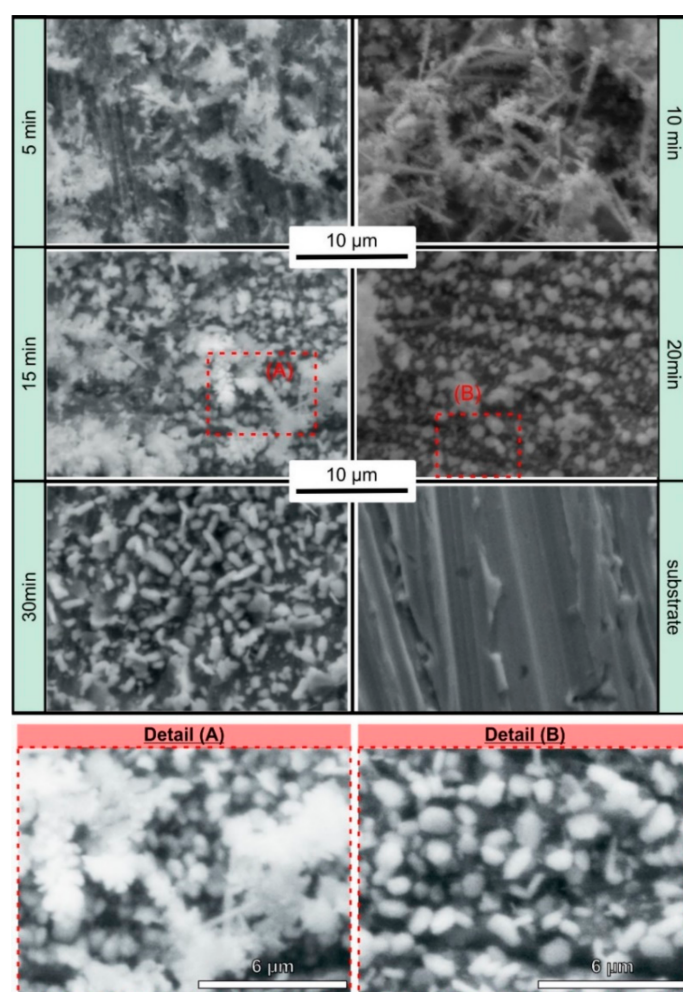


Figure 3. Scanning electron microscope (SEM) images of hydrophobic silver coatings produced using different immersion durations in silver nitrate solution and pH 10 for the Tris buffer solution.

It is known that the wettability properties of a solid surface depend on both the roughness and surface energy [35]. Roughness is a metric of surface topography which directly affects the contact angle values. Therefore, the parameters S_a , S_q , were calculated. S_a is the arithmetical mean height of the surface. S_q is the root mean square height of the surface. The 3D topography of the hydrophobic coatings is shown in Figure 4. The roughness increase was associated with the WCA growth following the same trend with respect to the immersion duration.

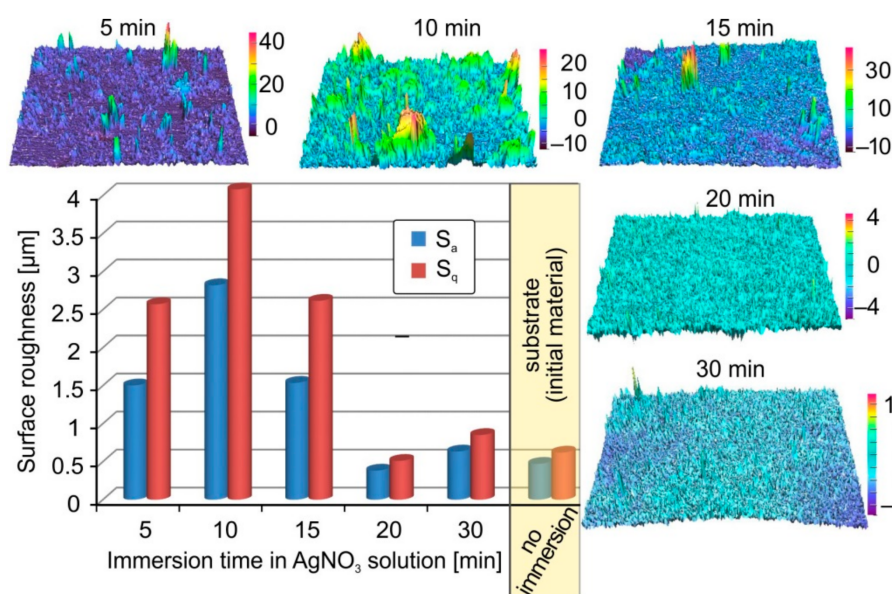


Figure 4. Surface roughness of silver-coated copper samples relative to the immersion duration in silver nitrate solution (using pH 10 for the Tris buffer solution) along with corresponding 3D imaging of surface topography.

When the immersion time in the silver nitrate solution was 5 min, the coating presented discontinuities. SEM images verified this observation since the copper substrate was visible (Figure 3). By increasing the immersion time to 10 min, the development of needle-like structures was observed, derived by self-organization of silver ions. However, the 3D topography of the surface revealed several clusters (of various sizes), indicating sufficient heterogeneity in the morphology of the coating (Figure 4).

Further increase of the immersion time to 15 min, gave rise to new morphologies and different topography of the coating produced. More specifically, a collapse of the agglomerates was observed whilst the needle-like morphologies almost disappear. Instead, dendritic or feather-like morphologies (see detail A of Figure 3) were distinguished. A second morphology was also pronounced, characterized by spherical agglomerates of approximately 1 μm. The results from the 3D topography for the silver-coated copper surface that was immersed in the silver nitrate solution for 15 min, indicated good homogeneity presenting only few large aggregates (Figure 4). When the immersion time increased to 20 min, the feather-like structures decomposed, whilst larger aggregates of Ag with polyhedral morphology, became visible. This morphology (polyhedral aggregates) was also visible for the samples that were immersed for 30 min in silver nitrate solution. As shown in Figure 4, for immersion duration higher than 20 min the silver coating was homogeneous and uniform. However, the roughness of this silver-coated copper surface decreased and resembled the roughness of the initial copper substrate which was attributed to the polyhedral and spherical structural morphologies of the coating. The hydrophobicity in this case diminished, with the WCA ranging from 140° to 143°.

The self-organization process for the Ag ions is well documented in literature [36–41]. Several mechanisms have been proposed while the reduction capacity of the substrate is stated as a key factor for the creation of dendrite-leaf morphologies [42]. In all cases the process begins with initial random reduction of Ag ions by the copper substrate and creation of nuclei that then grow to form primary nanoscale particles that further aggregate to form feather like structures or spherical morphologies. The immersion duration is also a significant factor that affects the 3D topography of the obtained silver coating (Figures 3 and 4) [36,40]. The SEM and micro-roughness results are consistent with the WCA measurements indicating that silver deposition time of 15 min is optimal to acquire a superhydrophobic silver film.

Figure 5a depicts a silver-coated copper sample produced under optimal conditions. The produced silver film exhibits good structural stability, superhydrophobic properties, (water contact angle of 152°) and displays an oleophilic nature.

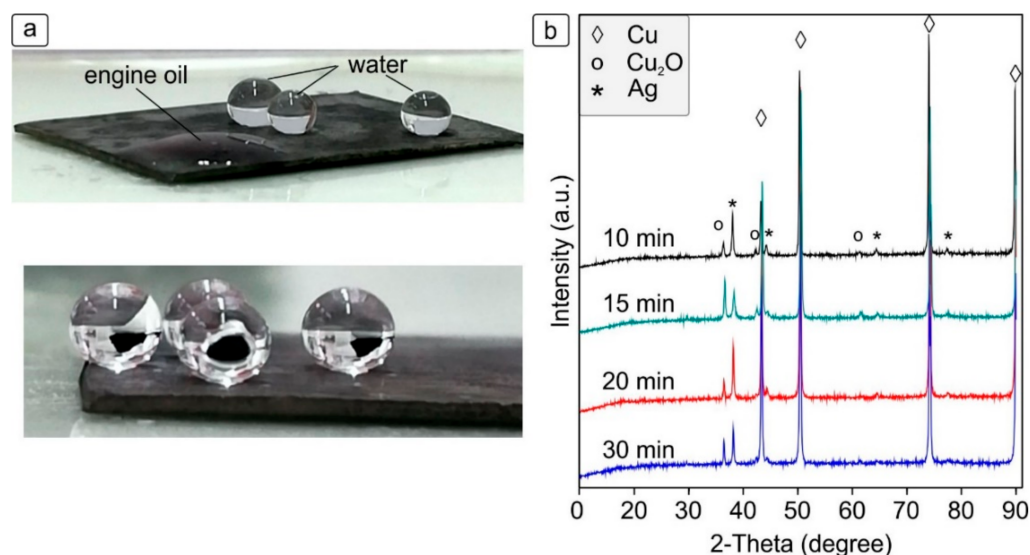


Figure 5. (a) Typical images of water droplets of about $6\ \mu\text{L}$ on the surface of silver-coated copper prepared under optimum conditions. (b) X-ray diffraction (XRD) results for hydrophobic silver-coated copper samples prepared under different immersion durations in silver nitrate solution and pH 10 for the Tris buffer solution.

XRD was used to examine the phases of the produced hydrophobic silver-coating under different immersion durations in silver nitrate solution and for pH 10 of the Tris-buffer solution. The XRD patterns revealed the presence of Ag for all immersion durations in AgNO_3 solution. Phases of Cu_2O oxide were also detected in all cases (Figure 5b), which probably can be ascribed to the decomposition of $\text{Cu}(\text{NO}_3)_2$ in copper oxide [34]. For all immersion durations the Ag diffraction peaks observed were the same, indexed as (111), (200), (220), and (311) planes of cubic Ag with a unit cell parameter equal to $4.0816\ \text{\AA}$. This result is consistent with the XRD results of previous works [34,43,44]. However, it should be noted that for immersion times of 20 and 30 min the (220) and (311) diffraction peaks were less intense and almost disappear indicating different growth mechanism of the Ag film at those immersion durations.

3.3. Electrochemical Corrosion Results

3.3.1. Polarization Measurements

All corrosion experiments were performed at silver-coated copper samples prepared under optimal conditions, e.g., at pH 10 for the Tris buffer solution and immersion time of 15 min in silver nitrate solution.

The OCP plots for the silver-coated copper and the bare substrate are shown in Figure 6a. After approximately 10 min of exposure a stable state of the E_{OCP} is reached. The corrosion potential (E_{corr}), corrosion current (i_{corr}), Tafel slopes, polarization resistance R_p and corrosion rate are presented in Table 1 whilst the polarization curves for the copper substrate and the silver-coated copper are shown in Figure 6b.

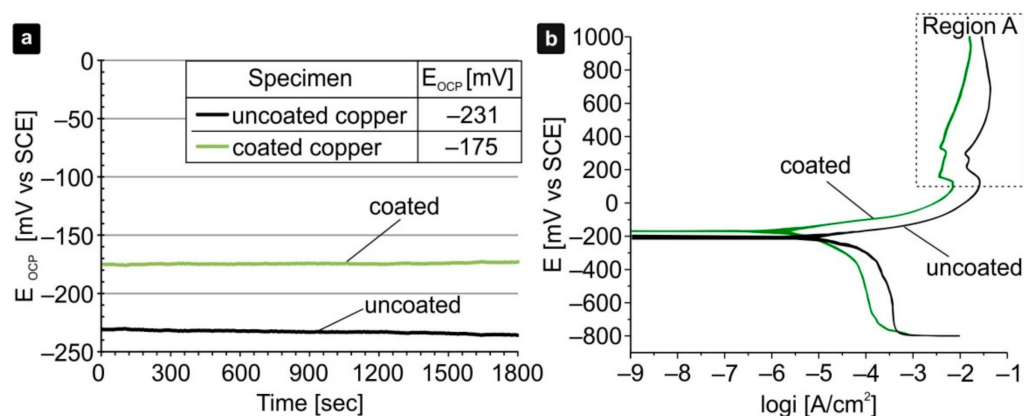


Figure 6. (a) Open circuit potential (OCP) and (b) polarization curves for silver-coated copper and copper substrate in 3.5 wt.% NaCl aqueous solution at a temperature of 25 °C.

Table 1. Polarization parameters.

Specimen	E_{corr} [mV]	i_{corr} [μ A/cm ²]	β_c [mV]	β_a [mV]	R_p [kohm/cm ²]	Corrosion Rate μ m/year
Copper substrate	−214	2	36.8	−53.7	0.82	24.06
Silver-coated copper	−170	0.5	38.3	−49.8	10.41	15.961

In terms of corrosion potential the silver-coated copper demonstrated a more electropositive (−174 mV vs. SCE) value than the uncoated copper (−214 mV vs. SCE). Regarding the current density i_{corr} , the silver-coated copper ($i_{corr} = 0.5 \mu\text{A}/\text{cm}^2$) displayed almost an order of magnitude smaller value compared to that of the copper substrate ($i_{corr} = 2 \mu\text{A}/\text{cm}^2$). Similar values for the current density i_{corr} of superhydrophobic copper were found in literature [12,15,21]. The values of the polarization resistance are consistent with those of the current density showing increased resistance for the silver-coated copper.

Both the reduced value of corrosion current i_{corr} and larger polarization resistance R_p indicated superior corrosion properties of the silver-coated copper sample. The superhydrophobic silver film, which was developed on the copper substrate, sifted the anodic and cathodic polarization curve to lower current densities, indicating thus an increased corrosion resistance. Concerning the anodic polarization part of Figure 6b an active dissolution nature is observed in both samples. However, as the potential rises the anodic current stabilizes and its values is independent of the voltage, suggesting an attenuation of the dissolution process (region A in Figure 6b). The anodic current density, at this region of reduced dissolution rate, is 50 times higher for the uncoated copper than that of the silver-coated copper (about 0.50 A/cm² for the uncoated copper and 0.01 A/cm² for the silver-coated copper). For the uncoated copper the two current density peaks apparent at the less active dissolution are ascribed to formation of Cu (I) and Cu (II) corrosion products probably due to reaction with Cl[−] as reported in literature [45]. The same peaks are apparent for the silver-coated copper; however, they are not so intensive. This might be an indication that the hydrophobic coating retards the dissolution of copper through the interface of the silver surface and finally to NaCl solution.

The WCA of the silver-coated copper sample after the polarization tests amounted of 142°. Compared to the initial WCA value of 152° only a 7% decrease was observed, indicating that the hydrophobicity loss was negligible. This observation could verify the existence of a reasonably stabilized air layer within the roughness of the silver-coated samples that was maintained throughout the entire polarization test. The formation of a relatively stable air film is considered as a sufficient corrosion protection mean since it leads to a reduced contact surface of the specimen with the solution [11–13].

3.3.2. Electrochemical Impedance Spectroscopy (EIS)

Impedance plots (Nyquist and Bode) may be used to evaluate the overall corrosion properties of materials as well as to elucidate the acting corrosion mechanism. The development of localized corrosion can be recognized in the kHz regions of the Bode plot, the global corrosion rate is related to the Hz zone while any adsorption of corrosion products or diffusion of ions is related to the mHz region of the Bode plot. [46,47].

For silver-coated copper, the Nyquist plot (Figure 7a) reveals a semicircle that begins at high frequencies and terminates at low frequencies, with the maximum imaginary value of impedance lying at 0.158 Hz (-33°). The total impedance of silver-coated copper approaches a distinct DC limit (15.85 kohm cm^2) at low frequencies (0.01 Hz) while at frequencies exceeding 10^3 Hz reaches a value close to 80 ohm cm^2 , according to the Bode plot (Figure 7b). The existence of a distinct DC limit may imply the absence of a diffusion process and pitting corrosion [47]. Two time constants for silver-coated copper are apparent at around 5.62 and 13.8 kHz, according to Bode plots. At phase angle–frequency curves, the existence of two or more time constants, together with a phase angle divergence from -90° , may suggest the development of inhomogeneous and irregularly dispersed reaction products on the sample surfaces [46,47].

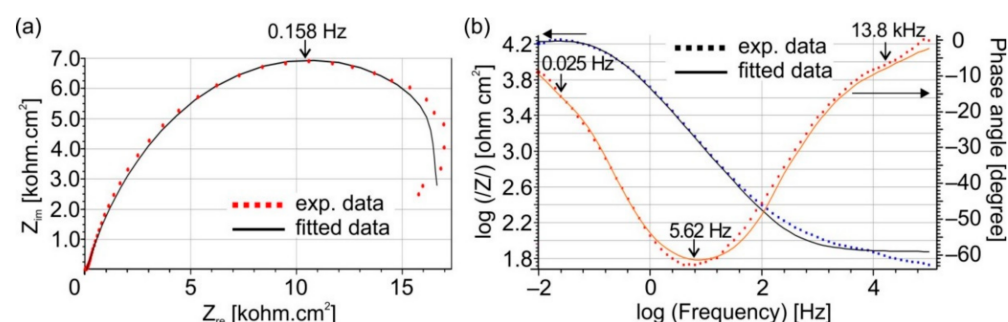


Figure 7. (a) Nyquist and (b) Bode plots of silver-coated copper in 3.5 wt.% NaCl aqueous solution.

For uncoated copper the Nyquist plots reveal a semicircle at high frequencies and a straight line at low frequencies (Figure 8a), which may be attributed to ion diffusion processes as well as any intermediate corrosion product absorbed on the specimen's surface [11,18,20]. High-frequency loops, in general, can be physically associated to the existence of corrosion products, whereas low-frequency loops can characterize the overall corrosion process [46,47].

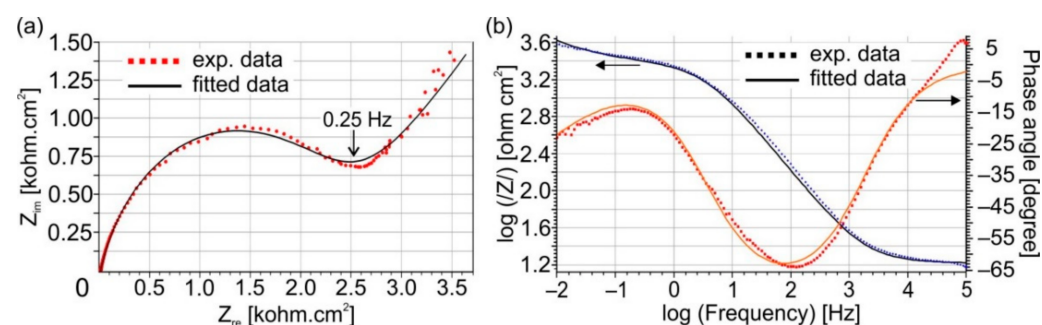


Figure 8. (a) Nyquist and (b) Bode plots of uncoated copper substrate in 3.5 wt.% aqueous solution NaCl.

At low frequencies (0.1 Hz), the slope of the impedance–frequency plot curve for uncoated copper (Figure 8b) remains stable, creating a continual rise in total impedance without establishing at an obvious DC limit. Furthermore, for frequencies higher than $10^{3.5}$ Hz, the impedance approaches zero value. The steady rise in impedance at low frequencies (below 0.1 Hz) confirms the presence of a diffusion mechanism that governs

the electrochemical reactions as well as the initiation of pitting corrosion on the test piece surface [46].

The Nyquist plots reveal that the hydrophobic silver-coated copper has higher ohmic and capacitive resistance (real and imaginary Z , respectively) which is connected with a decrease in corrosion rates. This result is consistent with the ones obtained by polarization measurements. The total impedance values of silver-coated copper are larger than those of uncoated samples. Finally, the total impedance–frequency curve tendencies corroborate with the results of Nyquist plots.

3.3.3. Proposed Equivalent Electrical Circuit Models

The corrosion behavior of hydrophobic surfaces in various solutions remains a major research topic and is well-documented in literature [10–16,18–23]. However, the simulation of experimental EIS data using equivalent electrical circuits that have a coherent physical interpretation remains a controversial issue. Hereupon, diverse models have been proposed in the literature for identical hydrophobic materials under similar corrosive conditions [15,18,20–23]. In any event, the goal of these simulations is to connect various electrical circuit parts to electrochemical processes that take place at existing or generated interfaces (e.g., metal/‘double’ layer/solution), providing better knowledge of the corrosion mechanism.

Two equivalent electrical circuits models are proposed (see Figure 9a,b) based on the microstructures, XRD analysis (Figures 3 and 4b) and impedance curves (Figures 7 and 8) of the silver-coated and uncoated copper samples. The goal was to minimize the number of elements used and simultaneously provide an appropriate fitting of experimental and simulated results. Additionally, the proposed models also provide the most rational and consistent physical interpretation of the results obtained.

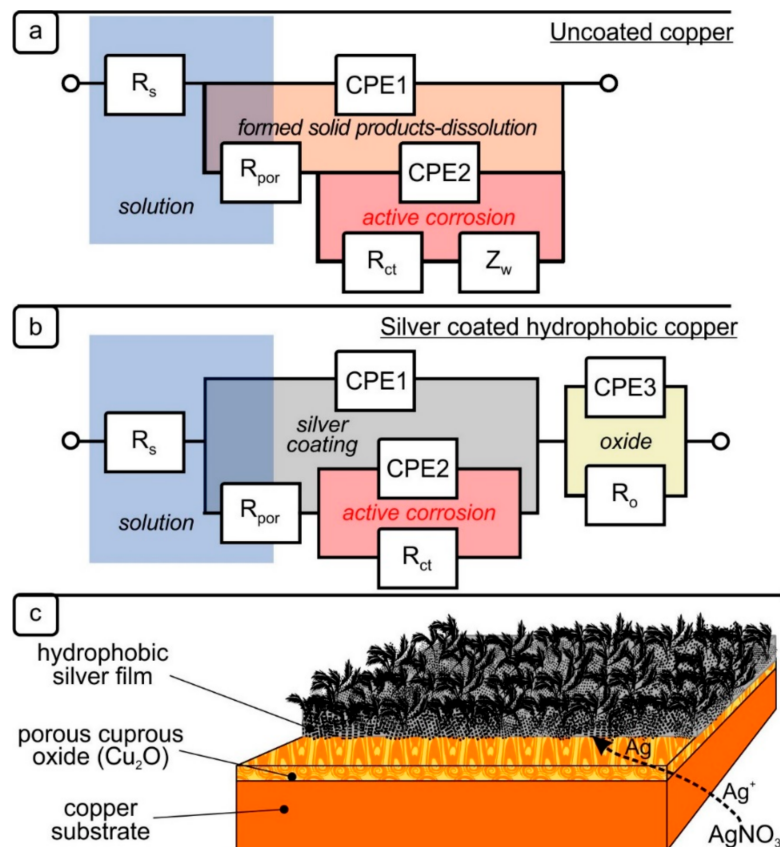


Figure 9. Proposed equivalent circuit representing the corrosion behavior of (a) uncoated copper and (b) silver-coated hydrophobic copper. (c) Schematic illustration of the silver coating structure used for representing the corrosion behavior of hydrophobic copper.

The proposed equivalent electrical circuit model for copper substrate (Figure 9a) comprises of: the electrolyte solution resistance R_s , a constant phase element CPE1 with an impedance Z_{CPE1} which represents the capacitance of the formed solid products on the surface of dense copper, the solution resistance R_{por} within a formed pore or pit on the solid surface related with solid product dissolution, a charged transfer resistance R_{ct} which characterizes the polarization of the copper due to the formation of the electric double layer on the interface between copper and the solution, a constant phase element CPE2 with impedance Z_{CPE2} which represents the capacitance contribution C_{dl} of the formed electric double layer on the interface between the copper substrate and the solution and a Warburg resistance Z_w related to the diffusion of the chloride ions and oxidants to the electric double layer on the interface between the copper and the solution.

Respectively, the proposed circuit for the silver-coated hydrophobic copper sample is that of the Figure 9b. It comprises of: the electrolyte solution resistance R_s , an constant phase element CPE1 with an impedance Z_{CPE1} which represents the capacitance C_C of the bulk silver coating (outside the pores), the pore resistance R_{por} represents the solution resistance within the formed pore and physically represents the ionic charge transfer through the aqueous or semi-aqueous pores and channels of the coating within the silver coating bulk, the C_C is the ability of the coating bulk to store charge, the R_{ct} charged transfer resistance which represents the polarization reaction between the copper–solution interface (inside the pore or channels that are formed) due to the electric double layer, an constant phase element CPE2 with an impedance Z_{CPE2} which represents the capacitance C_{dl} of the formed electric double layer between the copper–solution interface (inside the pore or channels that are formed). In terms of physical interpretation, this corresponds to current passing through the coating via ionic charge transfer, leading in either charge transfer across the interface (corrosion) or charge storage at the interface [21,22]. The R_o resistance characterizes the oxide layer of the silver-coated copper. The impedance Z_{CPE3} of the constant phase element CPE3 represents the capacitance C_O of the oxide layer which was detected through the XRD analysis.

Table 2 lists the parameters of the equivalent circuit elements of Figure 9. The fitting curves in Figures 7 and 8 are well adapted to the experimental ones, indicating that the proposed equivalent electric circuits are consistent with the experimental data (calculated standard error 6%).

Table 2. Best fitting parameters obtained using the proposed equivalent circuits, delineating the corrosion behavior of uncoated and silver silver-coated copper.

Material	R_s Ohm cm ²	R_{por} Ohm cm ²	CPE1		R_{ct} Ohm cm ²	CPE2		Z_w Ohm s ^{-0.5}	R_o Ohm cm ²	CPE3	
			$F \times s^{\alpha-1}$	α_1		$F \times s^{\alpha-1}$	α_2			$F s^{\alpha-1}$	α_3
Copper substrate	6.57	721	67×10^{-6}	0.82	717	228×10^{-6}	0.99	148	-	-	-
Coated copper	22.31	5446	110×10^{-6}	0.89	2229	1.96×10^{-6}	0.53	-	18.76	155×10^{-6}	0.62

A relatively homogeneous silver film covering almost entirely the copper substrate is reported according to the equivalent circuit model for the hydrophobic silver-coated copper. The relatively small divergence of coefficient α_1 from 1 suggests that the silver coating is fairly homogeneous (Table 2). There are, however, locations where metastable micro-pits or pores emerge that may facilitate the creation of active corrosion zones. Nevertheless, there is no evidence of significant ion diffusion (lack of diffusion resistance), which is most likely due to only locally scaled deterioration of the silver-coated coating. This means that the degradation of the hydrophobic film has not evolved to an extent that would allow chorine ions to freely penetrate the silver coating and move towards the metal surface indicating that a fairly stable air film was formed [18,21]. Additionally, any electrochemical reactions

of copper corrosion can be attributed only to an early stage of corrosion evolution and not to extended corrosion result.

These results are supported by the values shown of Table 2. More specifically, the value of Z_{CPE2} impedance is closely linked with active corrosion regions existing inside any created pore/pit. The decreased value for the silver-coated copper thus indicates enhanced corrosion resistance. The large divergence of α_2 from value 1 confirms the large instability of any formed corrosion products and the inhomogeneity of the electric double layer formed inside the pits.

For the silver-coated copper substrate the resistance R_{por} , associated with the solution properties, is one order of magnitude higher for the silver-coated copper indicating also that the interfacial coating properties in this case, play a dominant role in the evolution of corrosion. The higher values for R_{ct} for silver-coated copper indicate also superior resistance of the sample in general corrosion in relation to the copper substrate [11,18,20].

Finally, coefficient α_3 significantly deviates from 1 which indicates that the oxide layer is heterogeneous or has a porous nature (Figure 9c). The very low value of resistance R_o may indicate small thicknesses of the oxide thus allowing easy transfer of ions from the oxide layer through the copper substrate. Therefore it is suggested that the existence of the oxide layer does not contribute to any corrosion resistance.

4. Conclusions

Superhydrophobic silver coatings were successfully deposited on copper sheets substrates via immersion in chemical solutions. The surface morphologies were easily controlled by varying process conditions. The whole methodology is fast, simple and flexible. The influence of process conditions on wettability and the obtained silver film morphology and topography were examined and clarified. Under optimal conditions, a coherent silver coating with a dual morphology was produced, comprising of large regions with feather like structured and small regions with spherical morphologies. The produced silver-coated copper sheets were superhydrophobic and exhibited sufficient adhesion and stability. The superhydrophobicity of the silver coating derived from the synergistic effect of their surface microstructures and the modification with low energy groups of thiols. The superhydrophobic coating demonstrated enhanced anti-corrosion properties against NaCl aqueous solution in relation to the copper substrate as indicated from both EIS and potentiodynamic polarization experiments.

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