

Article



Cu–MoS₂ Superhydrophobic Coating by Composite Electrodeposition

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Abstract: In this work, a superhydrophobic coating was developed by composite electrodeposition of MoS_2 particles in a copper matrix. AISI 316L stainless steel and N80 carbon steel, with a thin electrodeposited Ni layer to improve adherence of the coating, were used as substrates. Different operational parameters of electrodeposition were studied in order to produce the highest possible contact angle. We demonstrate that, using this method, a coating with a hierarchical structure with feature dimensions in the range of μ m to nm is obtained, with advancing contact angle values up to 158.2° and a contact angle hysteresis equal to 1.8°. To study the coating composition energy dispersive X-ray, X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry were performed. Moreover, potentiodynamic polarizations were performed in H₂SO₄, NaCl and NaOH solutions to study the corrosion behavior of the coating. As a control, a sample coated only with MoS₂ particles by means of electrophoretic deposition was produced. The results show that the composite coating can be used in applications where copper is used for corrosion protection, with the addition of the desirable effects of its superhydrophobicity.

Keywords: superhydrophobic; composite electrodeposition; electrophoretic deposition; corrosion; composite coating; wettability

1. Introduction

Superhydrophobic surfaces have been widely studied in recent years due to their large variety of applications, and numerous methods have been developed for their fabrication. Such surfaces present a large range of properties, such as self-cleaning, anti-icing, low friction and corrosion protection [1,2].

Wettability is a result of the interaction between a solid surface and a liquid. As the name indicates, a superhydrophobic surface presents a low interaction with water, as the area that is wetted by the liquid is very small compared to the total area of the surface. A direct way of quantifying wettability is by measuring the contact angle: the angle that is formed between the solid surface–water interface and the side of a water droplet on the inner side. When analyzing a superhydrophobic surface, the advancing (θ_A) and receding (θ_R) contact angle should be measured; that is, the contact angle that forms when a water droplet is increasing and decreasing its volume, respectively. In this way, a superhydrophobic surface will present an advancing contact angle higher than 145° and a receding contact angle higher than 90° [3].

It is widely known that, for creating a superhydrophobic surface, two characteristics are necessary [2,4]; first, a rough surface and, secondly, a low surface energy. A water droplet must be in a Cassie–Baxter state (Figure 1a); that is, an air layer is entrapped in the rough surface, forming an air plastron and the contact between the solid and the liquid is very low; as a result, the droplet can roll freely on the surface. This free movement of the water can be very beneficial, as it can drag dirt from the surface, keeping it clean, for instance, for performing photosynthesis and breathing—this is

known as the "lotus effect" [5]. In this case, both θ_A and θ_R will have a high value and the contact angle hysteresis will be low. If the sample presents a high θ_A but the water droplet is in a Wenzel state (Figure 1b), in full contact with the surface, θ_R will be very low, and the droplet will not roll freely on the surface. Despite the high θ_A , this is not considered a superhydrophobic surface. This will be indicated by a low θ_R and, consequently, a high contact angle hysteresis.



Figure 1. Droplets in (a) Cassie–Baxter state and in (b) Wenzel state.

A rough surface in the micro/nano scale can be created using a number of different approaches [4]. However, in most cases, the material itself will not have a low surface energy, so an additional treatment will be necessary. Functionalization with molecule assemblies by means of self-assembled monolayers (SAM) is the most frequently used method for this aim. One example of widely used molecules which form SAMs are fluoroalkylsilanes (FAS), as they present a strong attachment to hydroxyl groups on metal and oxide surfaces, and an alkyl tail with low energy fluorinated groups [6,7]. There are also techniques that can be used to produce superhydrophobic surfaces in a one-step process. For example, plasma treatments can be used for depositing low surface energy materials directly with a rough structure—for example, fluorinated polymers [8]. In other cases, lasers can be used to create patterns in many materials' surfaces, such as various metals [9,10]. Controlling the atmosphere while the surface of the material is shaped can lead to surfaces with very different wettabilities [11]. These techniques can be used in simple steps and the surface morphology can be well controlled; however, they are also expensive and require special equipment.

Within the family of composite materials, metal matrix composites (MMC) are composed of particles of different materials, sizes and shapes in a metallic matrix. Composite electrodeposition is widely used for creating MMC coatings, and several application examples can be found in [12–14]. One of the main advantages of this fabrication method is that a coating can be made in a one-step process, as one can have all the components, such as the metal ion precursors and the particle suspension, in the same bath. Furthermore, it is very versatile because the process is of low cost and even allows for the coating of very intricate geometries.

Even though the required fabrication setup is simple, the mechanism involved is complex. The particles in the solution are charged because of the ions adsorbed on their surface or due to the addition of surfactant. These particles are physically dispersed in the solution and will move towards the cathode surface by a combination of convection and/or diffusion, but primarily because of the electric field. Once the particles are adsorbed on the surface, the metallic matrix that is growing due to the reduction in ions will physically embed the particles, leading to the formation of the composite coating. Its properties, such as particle/matrix ratio or its roughness, can be tailored by controlling the electrodeposition parameters.

Regarding superhydrophobic coatings, MMC gives the possibility of using particles of a low surface energy material and, therefore, an additional second step of functionalization is not required. Furthermore, the composite electrodeposition process can be tailored to control the roughness of the surface and the metallic matrix gives a good supporting structure for adherence of the particles to the surface. One example are the coatings developed by Zhao et al. demonstrating a Ni/WS₂ [15] and later a Ni/WC [16] superhydrophobic coating by electrodeposition, which combines the low wettability of transition metal chalcogenide (TMC) particles in a nickel matrix.

An interesting TMC material which also presents a low surface energy is MoS_2 . This material has a low cost and is commercially readily available, as it is typically employed as a lubricant due to its

layered structure which is similar to graphite. On the other hand, copper is a material that is relatively easy to electrodeposit compared to other metals and it presents a relatively good corrosion resistance in different media. Up to now, different coatings have been developed employing MoS_2 and other TMC particles in a metal matrix, such as nickel, chromium or copper. Most of these coatings were developed with lubrication as the main purpose. Furlan et al. [17] presents a good overview of different MMC coatings containing MoS_2 that have been developed for tribological applications. Stankovic et al. [18] studied the codeposition of MoS_2 particles and copper ions. Moreover, McGovern et al. [19] studied the stability of MoS_2 in contact with a copper matrix and confirmed that these coatings are stable, and the particles do not react with the copper matrix. This aspect is very important when choosing a combination of materials for a composite structure. Nevertheless, to the best of our knowledge, copper coatings with MoS_2 particles have not been created for low wettability purposes.

In this work, we developed a superhydrophobic metal matrix composite coating composed of MoS₂ particles in a copper matrix by means of composite electrodeposition. We evaluated morphology, composition, wettability and corrosion behavior in different electrolytes. As properties of composite materials are not a weighted average of the properties of the matrix and the particles, analyzing their properties may not be straightforward. For the aim of analyzing the corrosion behavior of the Cu–MoS₂ composite coating, following the work carried out by Panitz et al. [20], we produced a plain MoS₂ particle coating by means of electrophoretic deposition (EPD). Consequently, we could evaluate the corrosion behavior of a sample coated only with MoS₂ particles, a sample coated only with copper, and finally we compared the behavior of the Cu or MoS₂ coatings to the Cu–MoS₂ composite coating.

2. Materials and Methods

2.1. Sample Preparation and Cu–MoS₂ Coating

Stainless steel grade AISI 316L (SS 316L) and carbon steel N80 (CS N80) were used as substrates (see Table 1 for the nominal compositions). Both steels were cut in 1 mm × 20 mm × 20 mm square-shaped specimens. One side of the sample was ground with SiC from 320 up to 1200 grade, while the other side of the sample was painted with a non-conductive resin to insulate it and control the area to be coated. Finally, the samples were ultrasonically cleaned for 5 min in ethanol and dried with hot air.

Element	С	Si	Mn	Ni	Cr	Мо	S	Р	Fe
SS 316L	< 0.03	<1	<2	10	18	3	< 0.03	< 0.45	Balance
CS N80	0.31	0.19	0.92	-	0.20	-	0.08	0.01	Balance

Table 1. Nominal composition of stainless steel AISI 316L and carbon steel N80 used as substrates.

The coating procedure of the SS 316L substrate can be divided in three main steps. First, the sample was immersed for 20 s in a pickling solution (2.4 M HCl) to remove the native air-formed passive film. Subsequently, a thin nickel layer was deposited using Wood's nickel strike method (1.85 M NiCl₂ and 1.52 M HCl), with a current density of 35 mA/cm² for 3 min using a pure nickel anode and the sample as a cathode. The nickel thin layer was deposited on all samples to suppress surface oxidation and, hence, allow the electrodeposition of the Cu–MoS₂ coating. Finally, the sample was thoroughly rinsed with deionized water and the composite coating was deposited. The CS N80 substrate was coated directly with a nickel layer, using the same parameters that were used for the SS 316L substrate, and subsequently with a composite coating.

The preparation of the composite electrodeposition solution was performed as follows. $CuSO_4 \cdot 5H_2O$ and H_2SO_4 , according to [21], were diluted in deionized water in a volumetric flask (Solution A). In a beaker, 2 µm MoS₂ particles and cetyltrimethylammonium bromide (CTAB) were added to 40 mL of deionized water and ultrasonically stirred to create a suspension and hinder particle agglomeration (Solution B). Finally, Solution A, Solution B and thiourea [22] were added to a 200 mL

beaker that was magnetically stirred for 30 min. This beaker with the prepared solution was used for the coating electrodeposition (see Table 2 for final composition).

-	-
Components	Composition
CuSO ₄ ·H ₂ O	0.641 M
H_2SO_4	0.489 M
Thiourea	$5 \times 10^{-4} \mathrm{M}$
MoS_2 (2 μm particles)	2.5, 5, 10, 15, 20 g/L
СТАВ	0.1 g/g MoS ₂

Table 2. Composition of the Cu–MoS₂ electrodeposition solution.

CTAB (cetyltrimethylammonium bromide) is a cationic surfactant and it plays different roles in the solution: it allows the incorporation of the hydrophobic particles in the water-based suspension, it possesses a positive charge that hinders particle agglomeration and aids the movement of the particles towards the cathode. On the other hand, thiourea acts as a leveler and favors a coating that covers the entire surface, while the deposited particles and the current density can be adjusted to tailor the roughness of the coating [23–30]. Electrodeposition was performed with an electrochemical station (Zahner IM6, Kronach, Germany), with the sample connected as the cathode and a pure copper electrode as anode, both at a vertical position, while the solution was stirred by a magnetic stirrer at the bottom of the beaker. After the deposition of the composite coating, the sample was rinsed thoroughly with distilled water and dried in a nitrogen flow. Different concentrations of MoS₂ in the electrolyte and electrodeposition parameters were used to elucidate the optimal combination for obtaining the highest possible contact angle (see Tables 2 and 3).

Table 3. Different parameters used for electrodeposition of the composite Cu–MoS₂ composite coating using composition of Table 2.

Electrodeposition Parameters	Values
Current Density	40, 50, 60 mA/cm ²
Time	1, 2, 3, 5 min
Stirring	200 rpm
Temperature	Room temperature

2.2. Electrophoretic Deposition of a MoS₂ Coating

The stainless steel 316L substrates were coated with MoS₂ particles by means of electrophoretic deposition (EPD). The methodology developed by Panitz et al. [20] was followed, while solution composition and current density were adjusted to obtain a homogeneous coating on our samples. Here, we present the parameters that resulted in the best coverage, as our main goal was to obtain a MoS₂ coating in order to compare the corrosion behavior with our composite coating. The preparation of the substrate was the same used for the electrodeposited coatings; that is, the substrate was ground on one side, insulated with a non-conductive resin on the other side, and cleaned with ultrasonication in ethanol. The solution composition was 0.25 g/L MoS₂ particles (up to 2 μ m size) and 6.8 \times 10⁻⁴ M CTAB in deionized water. The MoS₂ particles were the same as used for the composite coating. The particles and surfactant were mixed in a volumetric flask and ultrasonicated for 20 min to stabilize and disperse the particles adequately. EPD was performed potentiostatically, applying 50 V for 30 s in a beaker with 80 mL of solution. The sample was the cathode and a platinum sheet was used as an anode with a fixed electrode distance of 1 cm. When the coating step was concluded, the sample was removed from the solution at a constant velocity to avoid gravity effects to damage the coating. Finally, the sample was annealed at 350 °C for one hour in a nitrogen atmosphere to calcinate the surfactant. The presence of surfactant was corroborated by XPS (results not presented in this paper) before and after annealing.

2.3. Sample Characterization

The morphology of the coating was first studied with a macroscope (Wild macroscope M420, Heerbrugg, Switzerland). More detailed images were obtained using scanning electron microscopy (SEM, Hitachi s-4800, Mannheim, Germany). The cross-section samples were fabricated with ion milling using argon ions and investigated using SEM. Qualitative composition analysis was carried out by energy dispersive X-ray (EDX, EDAX/TSL Genesis 4000, Weiterstadt, Germany), while composition analysis was performed by X-ray photoelectron spectroscopy (XPS, Physical Electronics 5600, Chanhassen, MN, USA) and time-of-flight secondary ion mass spectrometry (TOF-SIMS, ION-TOF GmbH—TOF.SIMS 5, Münster, Germany).

2.4. Wettability Characterization

The wettability of the samples was first screened using a static contact angle technique (Drop Shape Analyzer KRÜSS DSA30, Hamburg, Germany). Results from these measurements are presented in the Supplementary Materials, Table S1. From these results, the best samples were further analyzed, measuring θ_A and θ_R with the sessile drop-needle in drop technique (Dataphysics Contact Angle System OCA, Filderstadt, Germany) equipment, following the procedure detailed in [31]. The advancing and receding contact angle were calculated using the Young–Laplace fitting method, calculating the contact angle 20 times while the volume of the droplet was first increased and then decreased in four different spots in the center of the sample to avoid border effects. Then, the average and the standard deviation of the values were calculated.

2.5. Electrochemical Analysis

In order to perform a detailed analysis that allowed us to understand the properties not only of the composite coating, but also of its components, corrosion measurements were conducted on the following samples:

- 1. Stainless steel AISI 316L
- 2. Carbon steel N80
- 3. Stainless steel AISI 316L coated by EPD with MoS₂ particles
- 4. Stainless steel coated with a thin Ni layer and a Cu layer
- 5. Stainless steel AISI 316L with a thin Ni layer and a Cu–MoS₂ composite coating

The used solutions were 0.1 M H₂SO₄, 0.1 M NaCl and 0.1 M NaOH. A three-electrode configuration was used with the sample connected as the working electrode, a platinum electrode as a counter electrode, and an Ag/AgCl (3 M) as a reference electrode. The sample was in contact with the solution through a circular O-ring sealed opening exposing a circular area of 1 cm diameter. For each solution, open circuit potential measurement (OCP, Zahner Zennium Electrochemical Workstation, Kronach, Germany) was performed for one hour. The obtained OCP values are presented in Table 5, while complete plots are shown in the Supplementary Materials, Figure S1. As soon as the OCP measurement was concluded, potentiodynamic polarization was conducted at room temperature with a 2 mV/s scanning rate, from 300 mV below the recorded OCP value in the anodic direction. The electrochemical kinetic parameters, including the corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (βa) and cathodic Tafel slope (βc) were determined by linear extrapolations of Tafel lines obtained from 50 to 100 mV in the cathodic and anodic direction from the OCP. It is worth noting that, when performing electrochemical measurements, a comparable area between the different samples is needed so current densities can be compared. Because of this, CS N80 and SS 316L substrates were ground with SiC 1200 grade before electrochemical measurements, as this was the grade used in all the other samples previous to the coating deposition. This difference in the surface area should be taken into account when comparing the current densities.

Following the methodology presented in Section 2.1, it was possible to obtain a coating that covered the substrate surface homogeneously (Figure 2a) and presented a hierarchical coral-like structure (Figure 2b–e) composed of composite Cu and MoS₂ protuberances. The stainless steel substrate, the Ni coating, and the composite layers are clearly distinguished in the cross-sectional images in Figure 2d,e. It is interesting to note that the concentration of MoS₂ (black) in the coating affects its color. The higher the concentration, the darker the coating will be.



Figure 2. (a) Optical macrograph of a Cu–MoS₂ composite coating; (b,c) SEM micrograph of the coating in (a) showing a hierarchical structure; (d,e) SEM micrograph of a transversal cut done with ion milling of the Cu–MoS₂ composite coating; (f) images taken during advancing and receding contact angle measurements of the sample shown in (a) with θ_A equal to 158.2° and contact angle hysteresis 1.8°.

To analyze the composition of the coating, EDX analysis was performed (see Figure 3). The presence of copper, sulfur and molybdenum can be seen. The observed oxygen might be present as a result of copper oxidation after electrodeposition due to exposure to air, while iron may stem from the substrate and aluminum from the conductive glue used to fix the sample. The sulfur and molybdenum concentration could not be calculated due to the overlapping of their peaks. The XPS survey spectra (see Figure 4) confirm the presence of copper, molybdenum and sulfur on the surface. Peaks corresponding to carbon, bromine and nitrogen reveal the presence of surfactant, while carbon, nitrogen and sulfur may originate from thiourea.



Figure 3. EDX spectra of a stainless steel AISI 316L coated with a Cu–MoS₂ composite coating.



Figure 4. XPS survey spectra of a stainless steel AISI 316L coated with a Cu–MoS₂ composite coating.

The source of bromine is directly related to the presence of CTAB. To determine whether part of the carbon, nitrogen and sulfur could be correlated to the presence of thiourea compounds, TOF-SIMS analysis was performed. In the m/z 0–300 region of the positive ion spectrum (Figure 5), in the range of m/z lower than 60, hydrocarbon fragments of the surfactant can be seen, while signals of m/z values near 284 are principally assigned to complete surfactant CTAB molecules [32,33]. The values at m/z between 63 and 65 are attributed to the copper matrix [32].



Figure 5. TOF-SIMS ions with masses at the range of m/z 0 to 300 measured on the surface of a stainless steel AISI 316L coated with a Cu–MoS₂ composite coating.

As stated before, our aim was to find the parameters that allowed us to obtain the highest possible contact angle. Therefore, we performed the electrodeposition process using a wide range of values. For brevity, the contact angles obtained with different configurations are presented in Supplementary Materials, Table S1. For the rest of the results presented in this paper we used the parameters which yielded the highest contact angle (see Table 4).

Table 4. Advancing and receding contact angle with respective standard deviations and contact angle hysteresis obtained by composite electrodeposition of a Cu–MoS₂ coating on a SS 316L (A) and CS N80 (B) substrate.

Substrate	MoS ₂ in Solution (g/L)	Current Density (mA/cm ²)	Time (min)	σ _Α (°)	$\sigma_{\theta A}$	$ heta_{ m R}$ (°)	$\sigma_{\theta A}$	CA Hysteresis (°)
SS 316L	10.0	50.0	2.0	158.2	0.8	151.3	0.9	1.8
CS N80	10.0	90.0	2.0	151.6	0.4	149.6	0.3	2.0

For evaluating the viability of using this methodology for coating different ferrous materials, in addition to the stainless steel substrate, carbon steel N80 was also coated with the same methodology presented in Section 2.1. As with the coated stainless steel sample, the obtained morphology is comprised of a hierarchical coral-like structure (Figure 6). As can be seen in Table 4, the highest advancing contact angle and contact angle hysteresis obtained were 151.6° and 2.0°, respectively.



Figure 6. SEM micrograph of a Cu–MoS₂ composite coating on a carbon steel N80 substrate, (**b**) SEM micrograph of the coating in (**a**) with higher magnification.

As was discussed in the introduction, the morphology and surface energy of the coating, and therefore θ_A and θ_R , are related to the deposition parameters; however, a straightforward relationship with single parameters was not found. On the contrary, while most of the samples showed static contact angles higher than 100°, a wide range of parameters led to coatings with a static contact angle higher than 150°.

The total surface energy of the coating depends on the amount of MoS_2 particles incorporated, which is related to the particle concentration in the electrodeposition solution. For higher particle concentration in the solution, a higher potential was needed. However, this results in an accelerated hydrogen evolution, which can interfere with the desired morphology and homogeneity of the coating. Moreover, it was shown by Low et al. [12] that the number of particles in the coating increases with the particle concentration in the solution, until a saturation value is reached. The particle concentration in the solution, until a saturation value is reached. The particle concentration in the solution should be high, so a sufficient amount is incorporated for having a low surface energy; however, an excessive value is not necessary as, after a saturation point, the same amount will be incorporated into the coating. In our case, the concentrations that allowed us to obtain the highest contact angles were between 10 and 15 g/L.

On the other hand, the current density is related to the movement of metal ions and charged particles towards the cathode surface. If the current density is too low, the number of particles in the coating will be insufficient and it will also lead to a more even metal deposition, reducing the roughness of the coating.

Another important parameter is the solution flow rate, as it is responsible for the maintenance of the particle suspension and controls the movement of the particles towards the cathode for later entrapment in the metal matrix. As the electrodeposition was carried out in a glass beaker with a magnetic stirrer in the bottom, it was not possible to fully control the solution flow on the sample surface. We therefore assume that, when assessing the influence of different deposition parameters on the achieved contact angles, the lack of control of the hydrodynamic conditions was our main error source in this simple experimental setup. Furthermore, current density and solution flow rate are directly related to hydrogen evolution and to the removal of bubbles from the sample surface, as the deposition is carried out. The deposition time controls the size of the protuberances in the coating. As shown in Figure 2d,e, the cross-section of the sample indicates that a thin copper layer is first deposited and then the particle and copper protuberances grow on top of it. A deposition time lower than 30 s did not allow sufficient growth of the protuberances. On the other hand, depositions performed for longer than 4 min resulted, in the case of high MoS_2 concentration in the solution and high deposition current, in an excessive growth, and the optimal micro/nano structure for the superhydrophobic coating was lost.

It is well known that air diffusion towards the liquid due to surface tension phenomena leads to a change from the Cassie–Baxter to the Wenzel state and, hence, to the complete wetting of the surface [34]. To analyze this behavior, a sample was immersed in water (Figure 7) and pictures were taken every 10 s with a camera to record the evolution of the plastron. As can be seen in Figure 7a, the immersed surface appears with a brighter color, as it was illuminated in a way that meant the entrapped air layer reflected the light. A gradual disappearance of the reflecting layer was observed, and after 45 min the surface was completely wetted, indicating a transition between a Cassie-Baxter to a Wenzel state. It can be seen that the transition of wetting state begins in a circle-shaped area. This circle was likely created by a bubble formed during the nickel or the composite coating deposition process that was not removed from the sample surface. Consequently, this produced a change in the optimum hierarchical structure, leading to a line (the circle perimeter) where the Cassie–Baxter state was not stable. From this defect, the area that was wetted in a Wenzel state started to increase and, after 40 min, the entire surface outside the circle was completely wetted. Even though the air layer was lost after the immersion time, the three-phase contact line in the water surface did not advance significantly, so in this way a new part of the surface was not wetted. This confirms that the behavior of superhydrophobic surfaces will be different when the sample is immersed or when a single drop is deposited on top until it evaporates or slides away. This type of defect occurred only in some of the fabricated samples, especially when higher currents were used. If the deposition current is maintained in a low value, this kind of defect is not present. However, if the geometry of the sample does not allow for the complete removal of the formed bubbles, such defects are to be expected more frequently.



Figure 7. A superhydrophobic sample coated with a Cu–MoS₂ composite coating (Sample A from Table 4) immersed in water for (**a**) 0 s, (**b**) 10 min, (**c**) 20 min, (**d**) 30 min and (**e**) 40 min. A defect in the morphology can be noticed from (**b–e**) caused by a bubble formation and retention in the sample surface during the nickel or the composite coating deposition process.

The EPD-coated samples created for corrosion analysis presented a uniform particle deposition on the whole surface (Figure 8). A homogeneous gray color can be seen in Figure 8a, while Figure 8b,c show a smooth covering of the surface and the morphology of the particles is maintained. In the case of lower voltages and a higher distance between electrodes, a poor covering of the surface was observed. On the other hand, samples coated by applying higher voltages presented holes produced by bubbles that accumulated at the interface between the sample and the solution, because of the hydrogen evolution and the surfactant.



Figure 8. (a) Picture of the sample coated by EPD with MoS₂ particles, (b,c) SEM images of sample in (a).

As a first step, OCP measurements were performed using the methodology described in Section 2.5. The results are presented in Table 5 and the obtained plots in the Supplementary Materials, Figure S1. The OCP plots did not show any special "artifact" related to the transition between the Cassie–Baxter and the Wenzel state.

Table 5. Open circuit potential measurement (OCP) values after 1 h measurement and electrochemical kinetic parameters obtained from potentiodynamic polarizations presented in Figure 9, performed immediately after OCP measurements.

Sample	Solution	OCP (mV)	E _{corr} (mV)	i _{corr} (uA/cm ²)	βa (mV/dec)	βc (mV/dec)
SS 316L		-247	-302	4.4	-12,100 *	-93
Cu	01MH SO	151	21	15.2	55	1230 *
MoS ₂ (EPD)	$0.1 \text{ Im} 11_2 30_4$	327	237	2.9	162	-134
Cu-MoS ₂		371	-9	35.5	83	-150
SS 316L		-419	-468	2.6	345	-124
Cu	0.1 M NoCl	-128	-319	13.2	333	-99
MoS ₂ (EPD)	0.1 IVI INACI	141	33	11.9	148	-188
Cu-MoS ₂		-122	-287	18.7	182	-92
SS 316L		-523	-543	1.7	294	-123
Cu		-519	-559	17.1	53	-91
MoS ₂ (EPD)	0.1 M NaOn	-192	-289	8.3	289	-138
Cu-MoS ₂		-544	-561	296.7	77	-165

* It is important to point out that, in some cases, the shape of the polarization curve leads to values that present a higher error when calculating the Tafel lines by linear extrapolation.

Regarding the potentiodynamic polarization curves (Figure 9), the EPD-coated samples presented the most noble corrosion potential and a passivation range can be distinguished in the neutral and alkaline electrolyte. The noble corrosion potential was expected and is related to the fact that the stainless steel is covered by more noble particles and the catalytic effect of MoS₂ for hydrogen evolution [35]. On the other hand, the passivation range is due to the passivation of the stainless steel substrate, as it is evident that the electrolyte penetrates though the empty spaces between particles reaching the substrate. In the acidic solution, both the bare stainless steel sample and the MoS₂ EPD-coated one show passive behavior in terms of their corrosion potential. Upon anodic polarization, there is a slow increase in the anodic current densities for the EPD-coated samples that may be related to oxidation/dissolution reactions of MoS₂.

On the other hand, the composite $Cu-MoS_2$ coating presented a similar anodic behavior to the copper coating in all electrolytes. A comparison of the surface before and after potentiodynamic polarization in 0.1 M H₂SO₄ did not show a noticeable change in the morphology (Figure 10a,b), while the sample analyzed after polarization in 0.1 M NaOH solution (Figure 10c) shows $Cu(OH)_2$ needles, and the sample tested in 0.1 M NaCl solution was covered by a green layer (Figure 10d) which might be related to the formation of copper chlorides [36].

Current density (A/cm²)



Figure 9. Potentiodynamic polarization of a bare SS 316L substrate, SS 316L coated by EPD with MoS₂ particles, a copper coated sample and a composite $Cu-MoS_2$ in (a) 0.1 M H₂SO₄, (b) 0.1 M NaCl and (c) 0.1 M NaOH solution.

0.0

Voltage vs Ag/AgCl (V)

0.5

1.0

-0.5

1E-9 1E-10

-1.0



Figure 10. Composite Cu–MoS₂-coated samples (a) before and (b) after potentiodynamic polarization in 0.1 M H₂SO₄, (c) after polarization in 0.1 M NaOH, and (d) after polarization in 0.1 M NaCl.

When comparing the copper- and composite-coated samples, it is clearly seen that the catalytic effect of hydrogen evolution has a significant effect in the cathodic branch of the curves (especially in the H_2SO_4 solution). Taking into account the different roughness that each sample presents, a negative effect because of the rough hierarchical structure or a galvanic effect between the more noble particles and the copper matrix could not be seen. This finding indicates that the superhydrophobic coating can be used in applications where copper is used for corrosion protection, with the addition of the positive effects resulting from the superhydrophobic nature of the surface.

It is important to point out that potentiodynamic polarization exposes the samples to extreme conditions (full immersion, high potentials). Superhydrophobic surfaces are not intended for immersion, as it is well known that the Cassie–Baxter state is metastable and cannot be maintained for a long period of time. In the case of our experiments, the sample was immersed for one hour when performing OCP measurements, before the potentiodynamic polarization. However, in the case of droplets rolling on the surface, the interaction between the surface and the electrolyte is very low as the droplet slides freely, an effect that also leads to the so-called self-cleaning effect. How to retain the air plastron for a longer time is an open topic for future research.

4. Conclusions

In this work, a simple composite electrodeposition setup was used to fabricate a composite coating of MoS_2 particles in a copper matrix. The as-formed coating presented a lotus leaf-like hierarchical structure in the micro/nano range. This coating was successfully applied to stainless steel AISI 316L and carbon steel N80 substrates. Surface roughness and surface energy can be controlled by the electrodeposition process, the latter being dependent on the amount of MoS_2 particles in the coating. The coatings presented an advancing contact angle higher than 150° and a low contact angle hysteresis. Pictures taken during immersion testing showed the formation of an air plastron, formed due to the Cassie–Baxter state. EDX, XPS and TOF-SIMS surface analysis showed the presence of compounds originating from additives used in the electrodeposition bath. Corrosion experiments showed that the coating could be used in cases where copper is used for protection, with the addition of the positive properties gained from its superhydrophobic surface. Superhydrophobicity is expected to result in further protection, given the low interaction between the surface and harmful electrolytes in the environment.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-6412/10/3/238/s1, Figure S1: OCP measurements, Table S1: Contact angle of different samples.

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