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Eco-Friendly Superhydrophobic Graphene Oxide/Silica Coating by Cathodic Electrophoretic Deposition

Abadi, Mohammad Sadegh[1,*],
Hadavi, Seyed Mohamad Mahd[2]

[1] *Department of Corrosion and protection of Metals, Faculty of Mining and Materials, Tarbiat Modares university*
[2] *Department of Corrosion and protection of Metals, Faculty of Mining and Materials, Tarbiat Modares university*

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Abstract

Despite the unprecedented attention to the environmental impacts of coatings, no study has explored superhydrophobic coatings based on graphene oxide and silica. The present study aims to develop a low-cost, environmentally friendly method for producing superhydrophobic coatings to protect 5052 aluminum alloy. The main goal is to achieve hydrophobicity without relying on toxic secondary surface modification processes. In this regard, a two-step process including chemical etching (to create a hierarchical micro-nano structure) followed by cathodic electrophoretic deposition (EPD) from a suspension containing graphene oxide (GO) and silica nanoparticles (SiO_2) was employed. The raw materials and final coating were analyzed using techniques such as X-ray Diffraction (XRD), Hydrogen-1 Nuclear Magnetic Resonance (HNMR), Field-Emission Scanning Electron Microscopy (FE-SEM), Static contact angle (CA), Dynamic contact angle (DCA), and Fourier-Transform Infra-Red Spectroscopy (FTIR). The findings revealed a uniform “cauliflower-like” microstructure, with an average static contact angle of 162° and a residual contact angle of 4°, demonstrating superhydrophobic properties. FT-IR analysis revealed that the EPD process effectively reduced graphene oxide from its oxidized state and released hydrophilic functional groups on the surfaces of SiO_2 and graphene oxide. Two distinct bands are observed at wavenumbers 2857 cm^{-1} and 2903 cm^{-1}, which are assigned to the symmetric and asymmetric stretching vibrations of the methyl groups ($–CH_3$). These bands are related to the presence of $–SiOCH_3$ groups in the structure. These dual effects also made the coating naturally hydrophobic without needing extra steps, such as additional heat or chemical treatments.

Keywords

Coating
superhydrophobic
aluminum
eco-friendly

* Corresponding author: s.hadavi@modares.ac.ir
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1. Introduction

Environmental protection has become a major societal concern. Environmental problems, such as climate change, the greenhouse effect, acid rain, and the release of toxic substances, have far-reaching impacts on ecosystems and human societies. Accordingly, companies have increasingly designed products to preserve environmental resources while minimizing waste and environmental impacts [1]. Like other natural hazards such as earthquakes or severe weather events, corrosion can cause dangerous and costly damage to all industries, including pipelines, bridges, and public buildings, as well as vehicles, water and wastewater systems, hydrogen infrastructure, smart home and city appliances, electronics, batteries, sensors, and even nanotechnology equipment. However, unlike natural disasters, there are proven methods for preventing and controlling corrosion that can diminish or remove its effects on public safety, the economy, and the environment [2, 3]. Changes in weather and environmental factors significantly affect corrosion, and corrosion experts must understand their impacts. These factors include reducing carbon in various industrial sectors; atmospheric pollution; soil resistance; humidity and the impact of saltwater exposure on different material types; the kind of product to be processed, handled, or transported; the expected lifespan of the structure or component; proximity to corrosion-inducing factors; appropriate mitigation methods; and more [4, 5]. In recent years, the quest for new technologies to improve metal surface characteristics has become a major challenge in materials engineering, especially across diverse applications such as aerospace, automobile, marine, and electronics [6]. Among the different types of materials, Aluminum and its alloys are commonly used in various applications. Due to their low mass density, good mechanical behavior in addition to excellent corrosion resistance under a wide range of conditions [7]. However, these alloys are prone to corrosion in environments such as marine and industrial atmospheres. Consequently, protective measures are required to extend their service life and maintain performance. Although corrosion is a major issue for aluminum alloys, many conventional protective techniques raise environmental concerns [4]. This paper introduces a novel, green method for creating superhydrophobic coatings to protect aluminum alloys, with a focus on process sustainability.

Corrosion is defined as a damaging chemical or electrochemical reaction involving a material, typically metal, and its environment [8], and remains an ongoing problem with considerable economic repercussions. It is now estimated that the direct world cost of corrosion exceeds $1.8 trillion, and some 25–30% of it can be saved through proper management [2]. This phenomenon is particularly a major obstacle in the marine industry, where localized and general corrosion of aluminum alloys has limited their full commercial exploitation, despite numerous innovations [9].

Several methods exist to prevent metal corrosion across engineering applications. Currently, the primary metal protection methods include corrosion inhibitors, electrochemical protection, alloying, plating and spraying, and non-metallic coatings. In recent years, several coatings have been developed as corrosion inhibitors, though each presents specific limitations. For instance, fluorine-containing coatings have been associated with significant environmental impacts. Among the most recent developments are superhydrophobic coatings, which have attracted attention due to their low surface energy and water-repellent properties [10, 11].

The current industry standard for corrosion protection of aluminum often relies on chromate conversion coatings (CCCs) based on hexavalent chromium (Cr(VI)). Many scientific studies have identified Cr(VI) as a priority contaminant [12]. Additionally, many modern superhydrophobic coatings depend on a final modification step using fluorinated compounds (such as fluoroalkylsilanes or FAS) to attain low surface energy. These fluorinated compounds are now under review due to severe environmental concerns. Research shows that these materials can release persistent organic pollutants (POPs) such as PFOA[1] and PFOS[2] into the environment, which have the potential to bioaccumulate in living organisms and are known to be highly toxic [13].

Corrosion poses serious risks to the economy, human health, and the environment, making its prevention critically important. It is a major contributor to substantial global economic losses. Annual financial losses from metal corrosion exceed $100 billion, surpassing the combined costs of natural disasters such as hurricanes, floods, and fires [10]. NACE International, the world's largest corrosion association and a leader in corrosion protection, estimated the global losses due to corrosion at 2.5 trillion US dollars per year in a report published in 2016, which is equivalent to 3.4% of the global gross domestic product in 2013 [8]. Structural corrosion can result in severe injuries or even fatalities. Corrosion of aluminum alloys releases aluminum ions and other toxic substances into the environment, directly and indirectly impacting human health and ecosystems. While aluminum naturally occurs in air and water, human activities significantly increase its environmental concentrations [14]. Aluminum can exist in water in different forms and is affected by various parameters, such as pH, which determines the form of aluminum present in the aquatic environment. In studies that have investigated the level of aluminum in seafood, the results have shown that marine organisms can accumulate aluminum in their bodies and thus can be included in the life cycle and environmental health of living organisms and humans [15].

Even though corrosion reactions lead to the release of heavy metal ions, corrosion inhibitors used to date are toxic, and their excessive addition causes severe environmental pollution [10]. Corrosion Challenges on the Path to a Sustainable Society provides a body of information that demonstrates the importance of protecting metals and alloys from corrosion for industrial development and environmental sustainability.

One effective method for enhancing the corrosion resistance of aluminum alloys is to apply protective coatings to their surfaces. In this regard, superhydrophobic coatings inspired by nature, particularly those of lotus leaves, have attracted significant attention. Due to their high water contact angle and low surface energy, these types of coatings can prevent the entry of moisture and corrosive substances into the metal surface and provide desirable anti-corrosion performance [16].

Superhydrophobic surfaces have attracted the attention of many researchers owing to their unique properties, such as resistance to wettability and their high potential in diverse applications.

Corrosion-resistant coatings are essential for protecting metals from corrosive agents and are among the most effective methods for preventing surface degradation. Chromate-based systems, including primers and pigments, have long been among the most common and effective corrosion protection methods. However, due to environmental and human health risks, strict regulations such as the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) have been implemented [17, 18]. These regulations have restricted the use of hazardous compounds such as hexavalent chromium, volatile organic compounds (VOCs), and hazardous air pollutants (HAPs) in many industries [17, 19].

Today, production costs remain a major industrial priority alongside environmental concerns. Sustainability has also become a key criterion in material production, prompting the development and increased adoption of chromate-free coatings. Consequently, alternatives such as smart and green coatings have been developed, offering greater sustainability and reduced environmental impact [20].

Superhydrophobic surfaces exhibit water contact angles greater than 150 °. This property arises from the combination of two key factors: the presence of a waxy layer with low surface energy and rough nano- and microscopic structures. The self-cleaning properties observed in lotus leaves are due to the rolling of water droplets and the removal of surface contaminants. Many studies have been conducted to mimic this natural behavior and produce artificial superhydrophobic surfaces [21].

The properties and applications of superhydrophobic surfaces are generally divided into three main categories: self-cleaning, protective, and smart. These categories include properties such as self-healing, corrosion resistance, bio-anti-adhesion, and oil-water separation [22].

Table 1 provides a comparative summary of superhydrophobic coatings similar to those in the present study. Despite extensive research in developing superhydrophobic coatings, there has been a lack of studies on using graphene oxide and silica nanoparticles in such coatings for aluminum alloys through immersion and electrophoretic methods to improve corrosion resistance.

Table 1. Comparison of Superhydrophobic Coatings on Aluminum Substrates

Researcher(s)	Substrate (Alloy Type)	Coating	Contact Angle (°)	Sliding Angle (°)	Reference
Naghdi et al.	Aluminum	(rGO)	---	---	[23]
Xu et al.	Aluminum 6061	Nickel Stearate/Nickel Hydroxide	160 ± 1	2.1 ± 1	[24]
Naghdi et al.	Aluminum	GO/TiO_2	148	---	[25]
Khodaei et al.	Aluminum 1050	TEOS/GPTMS/Al_2O_3	164.3	2.5	[26]
Zhang et al.	Aluminum	Myristate/Aluminum	155.1	---	[27]
Zihao He et al.	Aluminum 5052	Dodecyltrimethoxysilane	155	---	[28]

[1] Perfluorooctanoic acid

[2] Perfluorooctane sulfonate

The main objective of the present study is to synthesize a superhydrophobic coating on 5052 aluminum using a combination of chemical etching and cathodic electrophoresis. In this regard, silica nanoparticles and graphene oxide have been used as key components in the coating process. The addition of silica nanoparticles has been made due to their unique properties, including increased surface roughness, reduced surface energy, and improved superhydrophobicity. Silica nanoparticles, by forming suitable nanometer-scale structures, increase the surface contact angle and thereby enhance the superhydrophobicity of the coating [29]. On the other hand, graphene oxide, due to its high chemical stability and layered structure, plays an essential role in improving corrosion resistance and increasing superhydrophobicity [30].

Compared with other coating methods, chemical etching and cathodic electrophoretic deposition are low-cost, non-toxic, and more environmentally friendly. Moreover, this method does not require complex or expensive equipment, relying on stable and readily available materials such as graphene oxide and silica. It also offers greater potential for industrial-scale implementation compared with many other advanced methods. The results of this research can contribute to a better understanding of how silica and graphene oxide nanoparticles enhance superhydrophobicity and can be proposed as an economical, biocompatible, and efficient solution to improve the durability and stability of aluminum alloys in corrosive environments.

2. Methodology

2.1. Material Preparation

Single-layer graphene oxide powder (purity 99%, 0.43-1.23 nm diameter, CAS: 7782-42-5) was purchased from US Nano Company. The XRD patterns clearly indicated that the only present phase was graphene oxide. (Figure 1)

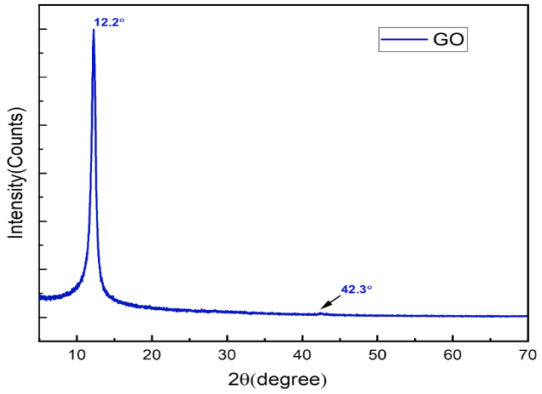

Figure 1. X-ray diffraction patterns for the obtained graphene oxide powder

Tetraethyl orthosilicate (TEOS) was used for the synthesis of silicon oxide. TEOS is one of the main precursors in the synthesis of silicon oxide due to its high purity and suitable hydrolysis ability.

To adjust the pH of the solutions, acetic acid (CH3COOH) was used; the etching solution was prepared from copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$), and for the laboratory processes of this research, high-purity laboratory-grade ethanol and acetone were used.

2.2. Sample preparation

Aluminum samples with 50×10×3 mm dimensions were prepared and used as the substrate. The chemical composition of the aluminum substrate used, determined by the quantitative method using the ASTM B209 reference standard, is reported in Table 2. The samples were sanded with sandpaper from 800 to 1200 grit, then washed in acetone and DI water for 10 minutes, respectively. Then, the cleaning operation was performed in an ultrasonic bath to thoroughly remove dirt and grease from the sample surfaces, preparing them for the next steps. In the next step, the aluminum samples were immersed in a 1 M copper chloride solution (CuCl2) for 15 seconds. This process was carried out to create a micro-nano structure on the samples' surfaces, providing the necessary conditions for the following stages of the research.

Table 2. Chemical composition of the substrate used in this study and 5052 aluminum alloy (wt%)

Element	Al	Si	Fe	Cu	Mn	Mg	Cr	Zn
Standard 5052 Alloy	Base	Max. 0.25	Max. 0.4	Max. 0.1	Max. 0.1	2.2-2.8	0.15-0.35	Max. 0.1
Used sample	Base	0.13	0.31	0.02	0.03	2.12	0.18	0.03

2.3. Preparation of the solution and performing the deposition process

To prepare the solution, graphene nanoparticles at a concentration of 0.5 mg/mL were carefully dispersed in water using an ultrasonic bath for 2 hours to achieve uniform distribution. Then, acetic acid was added to adjust the pH to 4. Finally, 1% by volume of tetraethoxysilane (TEOS) was added, and the solution was stirred until a completely uniform mixture was achieved. This solution was then used for the subsequent deposition step.

To perform the deposition process on the sample surfaces, 5052 aluminum samples were connected to the circuit as the cathode. A copper anode (with a purity of 99%) with similar dimensions to the cathode (10×50 mm) was used. The deposition process was performed using the pre-prepared solution of graphene oxide and TEOS from the previous step. The deposition was performed at 30 V for 3 minutes at ambient temperature. To ensure uniform particle dispersion, the suspension was sonicated in an ultrasonic bath for 30 minutes before deposition.

3. Results and Discussion

3.1. Structural measurement of silica nanoparticles

The silica nanoparticles were synthesized separately and analyzed to identify their functional and structural groups, as well as to understand the mechanisms underlying their effects. These results provide valuable insights into the reactions involved and aid in the synthesis of the superhydrophobic corrosion-resistant coating.

Figure 2 shows SEM images of synthesized silica particles. The particles are amorphous and homogeneous, providing a suitable structure and substrate for the adhesion of other particles and layers. These particles react with the graphene oxide layers and then settle on the aluminum sheets.

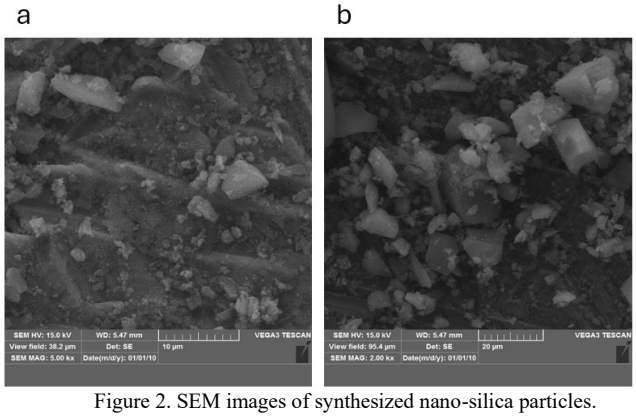

Figure 2. SEM images of synthesized nano-silica particles.

The HNMR test results of the synthesized silica, which were performed to identify the functional groups and chemical bonds, are shown in Figure 3.

Sixteen peaks were identified, among which several peaks were essential for determining the functional groups. The patterns in the range of 1.18 to 1.21 ppm are related to ethoxy groups (CH_3), those in the range of 3.3 to 3.33 ppm are associated with deuterated methanol (MeOD) as the solvent in the NMR analysis, whereas the patterns in the range of 3.6 to 3.63 ppm are related to ethoxy groups (CH_2), and finally the patterns in the range of 4.83 to 4.85 ppm are related to deuterated methanol (MeOD). The results of the integral ratio metric analysis of CH_3 to CH_2 groups are three to two, which is consistent with the expected chemical structure of the $-OCH_2CH_3$ group and confirms the presence of these groups in the structure of silica nanoparticles, as reported by others [31]. The presence of these hydrophobic groups will help create a superhydrophobic coating.

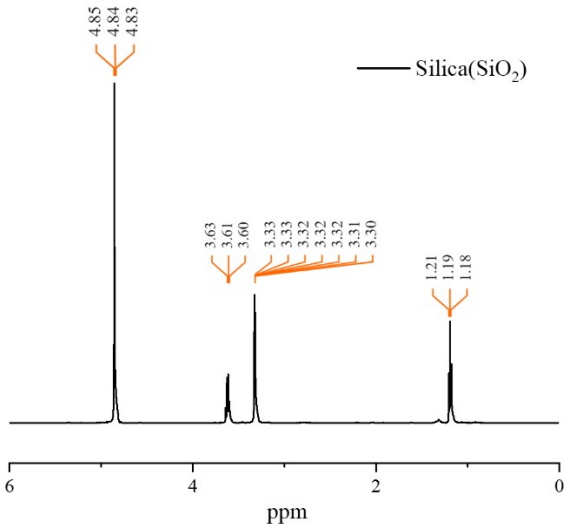

Figure 3. HNMR spectrum of synthesized nanosilica particles

The FTIR spectrum presented in Figure 4 confirms the successful formation of silica (SiO_2) nanoparticles by identifying their characteristic vibrational modes. The most prominent feature is a very strong and broad absorption band centered at approximately 1105 cm^{-1}, which is definitely attributed to the asymmetric stretching vibration of the siloxane (Si-O-Si) network [32]. This primary peak is complemented by two other key vibrations of the silica framework: a sharp peak at around 800 cm^{-1}, corresponding to the symmetric Si-O-Si stretching, and another band usually found near 470 cm^{-1} (visible on the right edge of the spectrum), which represents the Si-O-Si bending vibration [33]. The presence of all these bands in the FTIR serves as a primary fingerprint for the silica material.

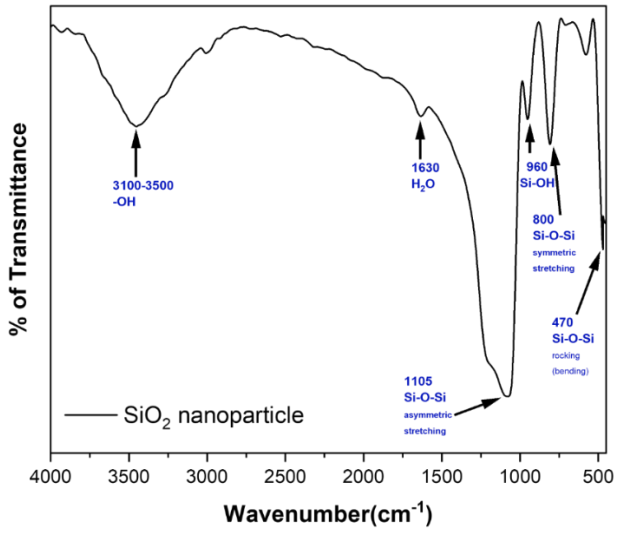

Figure 4. FTIR spectra of silica nanoparticles synthesized by the sol-gel method.

Furthermore, the spectrum provides essential information about the nanoparticles' surface chemistry. An extensive absorption band between 3100 and 3500 cm^{-1} is evident, which is attributed to the O–H stretching vibrations of both the surface silanol groups (Si–OH) and the physically adsorbed water molecules (H_2O) [32]. The presence of adsorbed water is evidenced by a distinct peak at around 1630 cm^{-1}, which is related to the bending (scissor) vibration of H–O–H. A key indicator of the nanoparticle surface is the peak or shoulder observed at around 960 cm^{-1}, which is specifically attributed to the Si–OH stretching vibration [32, 33]. The remarkable intensity of these hydroxyl and water-related bands is a characteristic feature of nanoscale silica, due to its high specific surface area and inherent hydrophilicity.

3.2. Superhydrophobic coating on 5052 aluminum samples

A two-step process was used to achieve a superhydrophobic coating on the samples. In the first step, chemical etching was performed to prepare and modify the surface. In the second step, an electrophoretic coating containing graphene oxide and silica was applied to the etched surface. Figure 5(a) shows the graphene oxide silane coating system, and Figure 5(b) shows the graphene oxide/silica coating applied to the aluminum substrate.

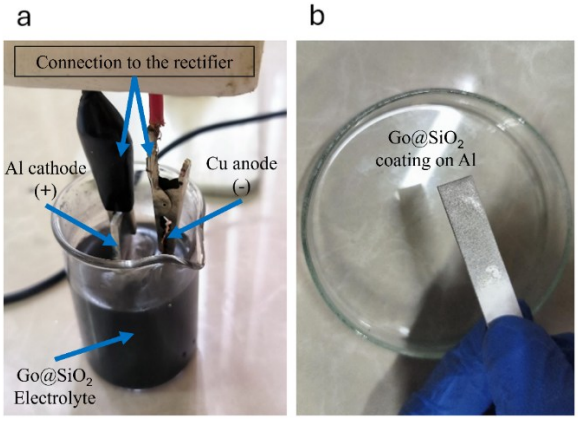

Figure 5. (a) Graphene oxide silane coatingsystem, (b) graphene oxide/silica coating applied to the surface of an aluminum substrate.

As Figure 6 shows the FE-SEM images of the polished surface of 5052 aluminum samples, no pits or ridges are left on the surface, whereas Figure 7 shows the etched surface of the samples after 15 seconds in 1 M copper chloride solution containing pits and ridges.

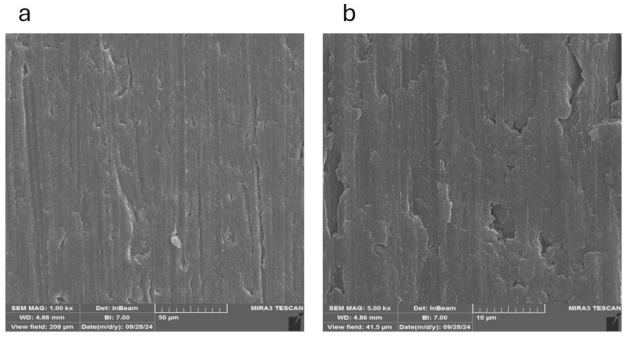

Figure 6. FE- SEM images of polished aluminum sample at different magnifications.

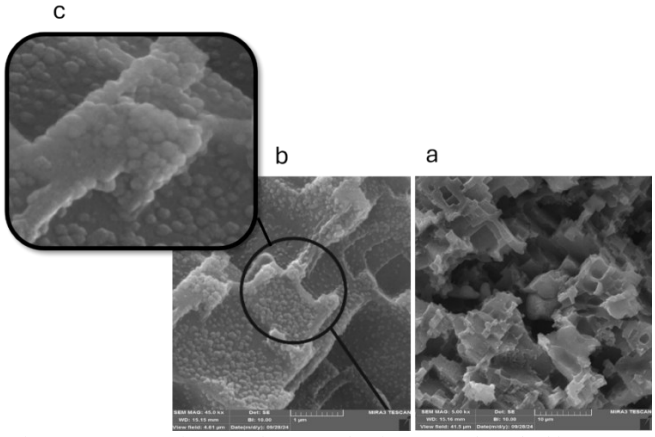

Figure 7. FE-SEM images of a 5052 aluminum sample etched in a 1M copper chloride solution for15 seconds.

After 15 seconds of immersion, the aluminum surfaces become fully etched, displaying irregular pits and ridges. At this stage, numerous rectangular platforms are uniformly distributed across the pits and ridges. Nanometer-scale step structures are also uniformly formed on these micrometer-scale platforms. Consequently, hierarchical micro- and nanoscale structures develop on the etched 5052 aluminum surfaces, markedly increasing surface roughness and providing an ideal substrate for subsequent coatings, consistent with previous reports [34, 35].

Figure 8 presents images from field emission scanning electron microscopy (FE-SEM) of the morphology of the superhydrophobic surface formed on 5052 aluminum after application of graphene oxide/silica coating. The coating was applied for 3 minutes on the etched aluminum prepared in the previous step.

As shown in Figure 8, after applying a graphene oxide/silica coating, a cauliflower-like structure has formed uniformly on the surface of 5052 aluminum alloy. In this structure, graphene oxide sheets are clearly visible.

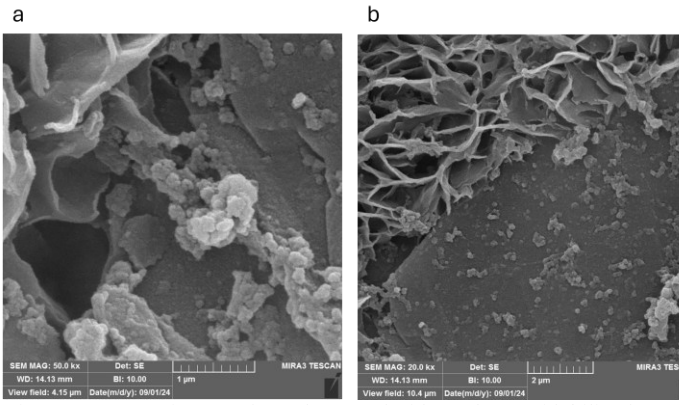

Figure 8. FE-SEM images of samples coated with graphene oxide/silica for 3 min at different magnifications.

Compared to the reported anodic electrophoretic deposition (aEPD) coatings [36-38], a completely different surface morphology was achieved in this study. In contrast to the smooth, uniform surface usually observed in anodic electrophoretic coatings, the coatings obtained by cathodic deposition in this study exhibit irregular, network-like topographies.

In addition, these changes may be due to a change in the synthesis protocol, which differs from conventional methods for graphene oxide/silica hybridization. These modifications in the protocol lead to the creation of a unique structure in the final coating and provide a specific morphology compared to conventional cathodic coatings [23, 25, 28]. The observed cauliflower-like structure can be due to the agglomeration of nanoparticles during the adsorption process in the synthesis step, which plays an essential role in the formation of this unique topography [39].

The FT-IR results of superhydrophobic coating of graphene oxide/silica nanoparticles on etched 5052 aluminum with a hierarchical micro-nano structure are presented in Figure 9. Silica (SiO_2), as a ceramic material, is naturally hydrophilic due to its high density of Si–OH groups and is used in various applications for surface manufacturing. However, these surfaces can become superhydrophobic at temperatures of 700 to 800 °C. This change is due to the reaction of Si–OH groups with one another and the formation of Si–O–Si bonds, which exhibit hydrophobic properties [40, 41]. One effective strategy to control the wettability of the SiO_2 surface during synthesis is to modify its surface chemistry via silane functionalization. This process leads to the formation of Si-$(CH_3)_3$ groups on the surface, resulting in a surface with controlled wettability and improved hydrophobicity [40, 42].

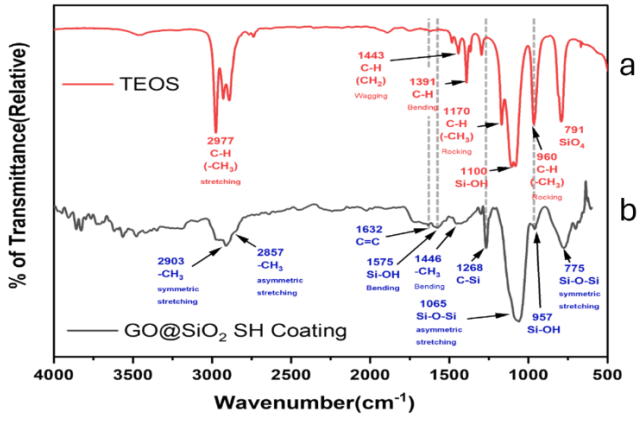

Figure 9. FT-IR spectra of (a) TEOS before hydrolysis; (b) the sample coated with graphene oxide/silica.

As seen in the results of FT-IR examinations (Figure 4) in methods such as sol-gel, the FT-IR spectrum usually shows a broad, strong band at 3148 cm^{-1}, because of stretching vibrations of –OH groups and the presence of Si–OH groups. According to the results obtained in Figure 9 the intensity of this band has decreased significantly, indicating a substantial removal of Si–OH groups from the surface. In Figure 9(a), The Fourier transform infrared spectroscopy before hydrolysis of tetraethyl orthosilicate (TEOS) shows that the peaks observed in the regions of 960 cm^{-1} and 1170 cm^{-1} are related to the hydrolysis process and the reduction of Si–OH bonds, which decrease in intensity with time and finally disappear. The presence of peaks at 965 cm^{-1} and 1065 cm^{-1} is related to the bending vibrations of Si-O-Si bonds, which indicate the formation of silicate structures during the polymerization process. This band confirms the formation of silicate ring structures and the increase in the density of the silica network during the process [43].

In addition, in Figure 9(b), the decrease in this band indicates that the hydroxyl groups present in the graphene oxide structure have also been significantly reduced, contributing to the chemical modification of the surface and increasing the hydrophobicity of the graphene oxide/silica coating. Two distinct bands are observed at wavenumbers 2857 cm^{-1} and 2903 cm^{-1}, which are assigned to the symmetric and asymmetric stretching vibrations of the methyl groups (–CH_3). These bands are related to the presence of –$SiOCH_3$ groups in the structure [40].

In addition, a band near 1446 cm^{-1} was also observed due to the bending vibration of the –CH_3 group [43]. Meanwhile, a prominent peak at 1065 cm^{-1} verifies the asymmetric stretching vibration of Si–O–Si. It also shows a peak at 957 cm^{-1} for the Si–OH stretching vibrations and one at 755 cm^{-1} for the symmetric Si–O–Si stretching vibration [44].

In Figure 9(b), the band observed at 1268 cm^{-1} was attributed to the C–Si bond. This observation, in addition to the spectral changes reported herein, supports the notion that the graphene oxide/silica hybrid nanoparticles have been modified by replacing protic/acid groups (e.g., hydroxyl and carboxyl) with nonpolar Si–C and C–H bonds. This surface modification not only leads to the formation of a durable hybrid coating, but also significantly improves the hydrophobicity of the graphene oxide/silica coating [42, 44, 45].

Also, the peak observed at wavenumber 1632 cm^{-1} is associated with the skeletal vibration mode (corresponding to the motion of carbon atoms in the graphitic (sp^2) structure) in the intact graphitic regions in the basal plane of graphene sheets, indicating the preservation of the graphitic structure in some areas of the graphene oxide sheets [46].

In addition, during the electrophoretic coating, graphene oxide can be reduced through two mechanisms: hydrogenation and hydrogenolysis. This process changes the coating's surface chemistry by removing the protic functional groups on the graphene oxide surface and converting it to reduced graphene oxide. The reduction of groups such as hydroxyl in Fourier transform infrared (FT-IR) spectroscopy also confirms this, not only for graphene oxide but also for silica nanoparticles [39, 45].

The residual water contact angle is a key parameter for characterizing and evaluating superhydrophobic surfaces. For this reason, this test was performed on the samples according to the ASTM D7334 standard to analyze surface properties more accurately. The results obtained in Figure 10 showed that the average residual contact angle, which represents the difference between the advancing and receding contact angles, is equal to 4 degrees for these surfaces. This low value indicates the surface's strong super-hydrophobicity and reduced adhesion of water droplets. The average contact angle is also determined to be 162 degrees. In contrast, on polished aluminum, due to the surface's hydrophilic nature, the average contact angle is 55.1 degrees, as shown in the figures.

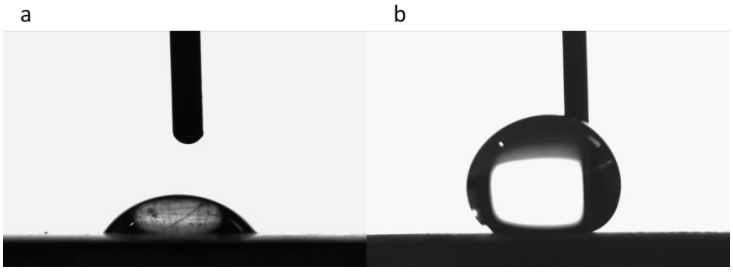

Figure 10. Contact angle tests on the aluminum samples, (a) as-polished sample; (b) with graphene oxide/silica coating.

4. Conclusions

In this study, the main objective of creating an innovative superhydrophobic coating on 5052 aluminum alloy was successfully achieved. This achievement was accomplished using an electrochemical method (cathodic EPD) based on a graphene oxide-silica composite. The most important innovative aspect of this work is achieving high superhydrophobicity without the need for any secondary surface modification with environmentally harmful materials. In this synthesis method, the electrophoretic process simultaneously reduced graphene oxide and removed hydrophilic functional groups from the coating surface, thereby replacing conventional high-temperature or chemical processes.

This achievement provides a ‘green route’ for metal protection. The method avoids two toxic industrial approaches: chromate-based coatings and those requiring fluorinated compounds. The EPD process is inherently eco-friendly, conducted in an aqueous solution without emitting volatile organic compounds (VOCs). This study offers a practical, low-cost, and scalable solution that aligns with global ‘green chemistry’ goals. By eliminating toxic surface modifications, it addresses environmental and industrial concerns in metal protection. While the method shows strong laboratory-scale potential, several challenges must be overcome for industrial implementation. Key scalability challenges include maintaining long-term bath suspension stability to prevent particle aggregation and achieving uniform coatings on complex geometries. Finally, this green protocol

should be tested on other widely used engineering substrates, such as magnesium alloys and steel.

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