*Journal of Metals, Materials and Minerals, 35(4), e2217, 2025*

# Coating of zinc substrates with fluorosilane molecules using a water-treatment technique as a pre-coating procedure for the creation of superhydrophobic surfaces

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**Received date:**
29 November 2024
**Revised date:**
2 July 2025
**Accepted date:**
23 September 2025

**Keywords:**
Organosilane;
Molecular coating;
Superhydrophobicity;
Functionalization;
Water contact angle

**Abstract**

Superhydrophobic surfaces were successfully created when zinc substrates were coated with molecules with low surface energy through grafting of fluorosilane molecules. The zinc substrate underwent water-treatment technique as a pre-coating procedure to enhance the reaction sites for the grafting of fluorosilane molecules. The water contact angle of the samples went as high as 161.1° ± 0.8°. At lower fluorosilane-ethanol soaking times, water contact angles have lower values while at higher soaking time, it has higher water contact angle values. At 240 min fluorosilane-ethanol soaking time, optimum value of water contact angle was achieved. Fluorosilane molecules are widely distributed through the zinc substrate surface as inferred from the mapping of the silicon atoms through Energy Dispersive Spectroscopy. As inferred from the Infrared Spectroscopy, water treatment process enhances presence of Zn–OH moieties which are perceived to be binding sites of fluorosilane molecules. The presence of vibrational modes related to Si–O and C–F were detected after the water-treated samples were soaked in fluorosilane-ethanol solution; the said vibrational modes were attributed to the presence of grafted fluorosilane molecules.

## 1. Introduction

Metal with superhydrophobic surfaces is eyed for various applications [1-12] (such as for self-cleaning, anti-fouling, anti-icy, anti-friction, anti-fogging, and anticorrosion) in different fields such as biomedical, energy, industry. Superhydrophobicity is exemplified by a surface when a water droplet on it has contact angle is 150° or higher. At this contact angle, the water droplet is near spherical, thus it is capable of rolling at a surface with a slight angle of inclination. Rolling water droplets on a surface can adhere with loosely adhered dirt, thus enabling cleaning the surface; thus, the term self-cleaning was coined. Furthermore, a superhydrophobic surface has low adherence to a wide variety of materials, such as fog, ice, and biofouling materials. Superhydrophobic surfaces' low adherence with a wide variety of material also entails it to have less friction with a variety of surfaces it is in contact with.

A technique to create metals with a superhydrophobic surface is by coating molecules with low surface energy such as fluorinate organosilane molecules. An organosilane molecule has a surface-reactive head and a surface inert tail carrying the functional group. The reactive heads of organosilane molecules can react and orient toward the surface of a substrate while a surface-inert tail with low surface energy can point away from the surface. The said configuration enables the creation of a molecular coating in which the innermost portion is chemically bonded on the surface of the substrate while the outermost portion has superhydrophobic properties.

Several literatures presented research on placing organosilane molecules on metal surfaces or materials on metal surfaces to improve the water contact angle or achieve superhydrophobicity [13-18]. Coating organosilane molecules on metal surfaces is usually preceded by pre-coating treatment such as acid or base treatments [19-27]. However, these commonly used methods exhibit possible limitations or disadvantages such as danger of using acids and base. One possible simple alternative technique is to add water molecules on the metal surface; the presence of water molecules can introduce hydroxyl moieties on the metal's oxide layer in which the organosilane molecules can react and chemical bind. The use of a simple water-treated method at room temperature would enable upscaling of the coating process for mass production simpler by avoiding challenges with regards the disposal of acid or base or the use of heat treatment facilities.

The main objective of this study is to coat fluorosilane molecules (a type of organosilane molecules with low surface energy tail) onto a zinc substrate using a room temperature water-treatment technique as a pre-coating procedure to produce superhydrophobic surfaces.

## 2. Experimental

### 2.1 Materials

Zinc sheets with 10 mm × 10 mm × 0.5 mm dimension was used as substrates; these were cut from a PTPTRATE zinc sheet with an initial

dimension of 10 mm × 10 mm × 0.5 mm. A silicon carbide grit paper (P1000 Supermova) was used to roughen the substrate. Fluorosilane molecules (1H,1H,2H,2H-Perfluorodecyltriethoxysilane, Sigma Aldrich 97%) were used as coating agents and absolute ethanol (ChemSupply) as their coating medium.

### 2.2 Pre-coating procedure using a water treatment method

Zinc substrates were soaked in water inside a petri dish; wherein the water level was just above the surface of the substrate. The set-up was left until there was no water inside the petri dish visible to the naked eye.

### 2.3 Coating of substrate using a simple soaking technique

The water-treated substrates were placed inside a 30 mL beaker containing 5 mL of fluorosilane-absolute ethanol solution (1% v/v). Absolute ethanol was used to minimize the amount of water in the bulk of the solution; water molecules may trigger reactions of fluorosilane molecules with each other. The substrates were soaked for 1 min, 5 min, 10 min, 15 min, 60 min, 240 min, 1440 min. After soaking, the fluorosilane treated substrates were left to air dry for one week.

### 2.4 Characterization

The water contact angle of the sample was determined using Sessile Drop Technique. The infrared spectra of the samples were determined using Shimadzu IR Prestige-21 Fourier Transform Infrared (FTIR) Spectrophotometer with Attenuated Total Reflectance (ATR) mode. The elemental map of the sample was determined using Field Emission Scanning Electron Microscope (Dual Beam Helios Nanolab 600i) equipped with Energy Dispersive Spectrometer (AL-TP-104 Elemental Analysis).

## 3. Results and discussion

We are successful in creating superhydrophobic surfaces using a simple water-treatment technique as a pre-coating procedure (Figure 1). As such, the water contact angle of the sample that underwent water-treatment technique as a pre-coating procedure before soaking in fluorosilane-ethanol solution was 161° ± 1°; this value is larger than the sample that did not undergo water-treatment technique as a pre-coating procedure (113° ± 6°) and much larger than the zinc substrate water contact angle (90° ± 6°).

The water contact angle of samples that underwent water-treatment technique as pre-treatment procedure before soaking in fluorosilane-ethanol solution went as high as 161.1° ± 0.8° (Figure 2) at fluorosilane-ethanol solution soaking time of 240 min. At lower fluorosilane-ethanol soaking times (1 min to 10 min), only hydrophobic surfaces were formed; meanwhile at higher soaking times (5 min to 24 h) superhydrophobic surfaces were formed. Note that water contact angles of all samples that were soaked in fluorosilane-ethanol solution improved. Furthermore, the water contact angle of the samples did not vary much after one month and two months.

Table 1 shows the water contact angle of different zinc substrates, which undergoes different coating, functionalization or surface modification processes. All of the mentioned processes yielded water contact angles greater than 150°, signifying all of them have super-hydrophobic surfaces. The maximum possible water contact angle yielded in this research is either comparable, lower or greater than that of listed in the table. However, the advantage of the methods in this research is the simplicity of the process which involves the use of water pretreatment at room temperature before grafting with functional molecules. Water pretreatment methods in room temperature do not need the use of specialized equipment (such as autoclave, electro-chemical set-up) or reagents other than water.

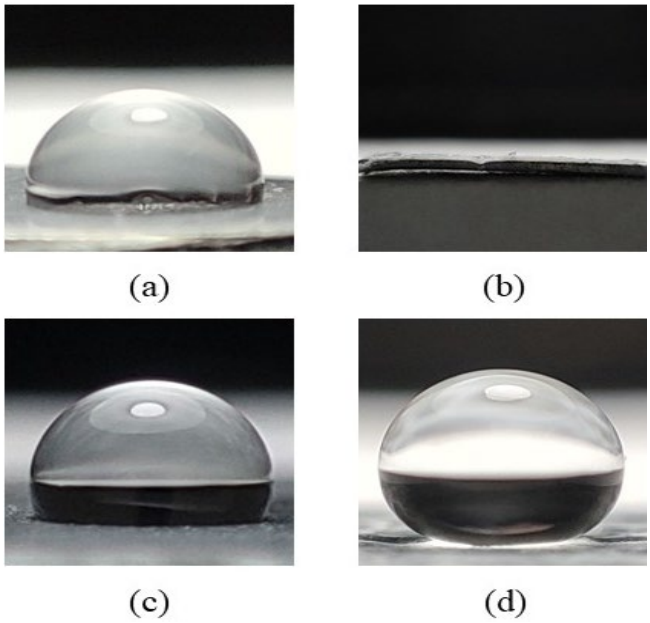


**Figure 1.** Representative water droplets on different surfaces with corresponding water contact angle: (a) zinc substrate, 90°, (b) water-treated zinc substrate, 0° (c) zinc substrate soaked in fluorosilane-ethanol solution for 24 h without water treatment technique as a pre-coating procedure, 113° and (d) zinc substrate which underwent water treatment technique as a pre-coating procedure then soaked in fluorosilane-ethanol solution for 24 h, 161°.

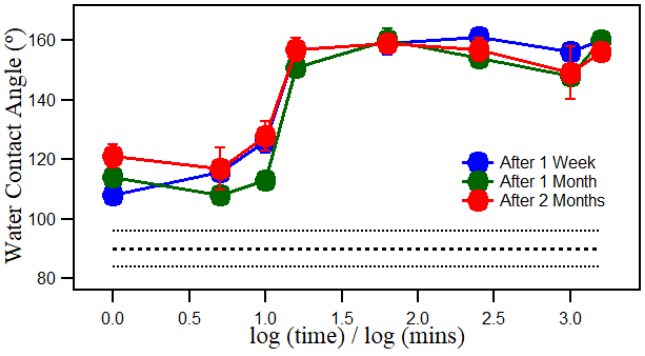


**Figure 2.** Water Contact Angle of samples that underwent water treatment technique as a pre-coating procedure before soaking in fluorosilane-ethanol solution at different soaking times. The dotted middle line pertains to the water contact angle of the untreated zinc while the upper and lower dotted lines represent the uncertainties.

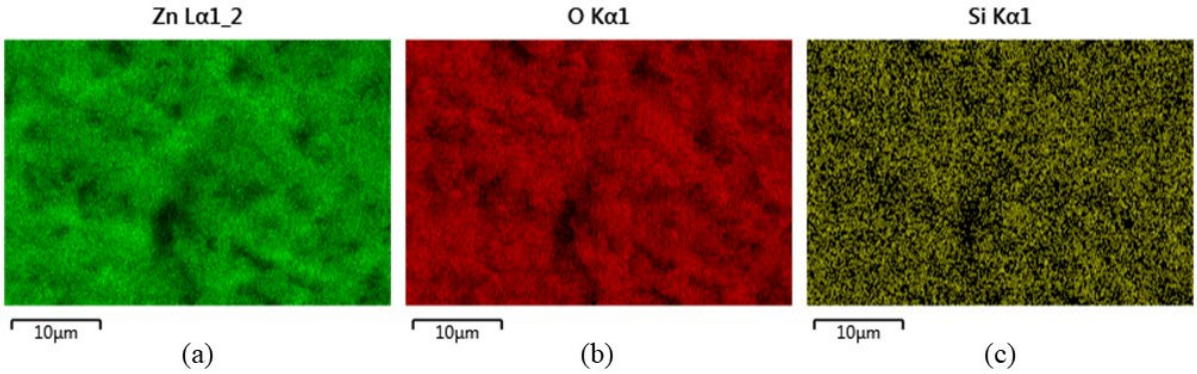


**Figure 3.** Map of (a) Zinc, (b) Oxygen, and (c) Silicon atoms on samples that underwent water treatment technique as a pre-coating procedure before soaking in fluorosilane-ethanol solution as viewed in Energy Dispersive Spectroscopy.

**Table 1.** List of studies of superhydrophobic zinc substrates with its corresponding functionalization or modification processes and water contact angle.

| Zinc substrate coating, functionalization or modification processes | Water contact angle |
|---|---|
| Water-only hydrothermal process and modification with Actyflon-G502 ($CH_3(CF_2)_6(CH_2)_3Si(OCH_3)_3$) [28] | 156° |
| Polydopamine (PDA) surface modification and treated with 1H, 1H, 2H, 2H-perfluoromethyl mercaptan (PFDT) [29] | 161° ± 3° |
| Electrochemical process with fluoroalkylsilane treatment [30] | 165.3° |
| $AgNO_3$ and octadecyl mercaptan solution treatment[31] | 161.2° |
| Water pre-treatment (at room temperature) and surface functionalization with fluorosilane molecules (This work) | 161.1° ± 0.8° |

**Table 2.** Assigned Vibrational Modes of the Infrared Spectra in Figure 4. Labels are as follows: "A" is for zinc substrate, "B" is for zinc substrate that underwent water-treatment, and "C" is for zinc substrate that underwent water treatment technique as a pre-coating procedure before soaking in fluorosilane-ethanol solution.

| Vibrational mode | A | B | C |
|---|---|---|---|
| Zn–OH bending | | 1497 | 1499 |
| O–Zn–OH bending | | 1385 | 1373 |
| F–CF stretching | | | 1238 |
| $F_2$–CF stretching | | | 1204 |
| Si–O–Si asymmetric stretching | | | 1146 |
| O–Si–O–Si asymmetric stretching | | | 1136 |
| Zn–O–Zn asymmetric stretching | 1049 | 1042 | |
| O–Zn–O–Zn asymmetric stretching | 1043 | 947 | |
| Zn–O bending | | 829 | 827 |

Figure 3(a-b) show the map of zinc atoms and oxygen atoms on samples that underwent water treatment technique as a pre-coating procedure before soaking in fluorosilane-ethanol solution as viewed in Energy Dispersive Spectroscopy. The distributions of zinc atoms (Figure 3(a)) and the distribution of oxygen atoms (Figure 3(b)) on the substrate are quite similar. The said similarity may indicate 1:1 correspondence of zinc atoms and oxygen atoms, which may suggest the presence of ZnO or Zn–OH on the top of zinc substrate. The slight differences in the distribution of oxygen atoms from zinc atoms might be due to the presence of adventurous oxygen-based molecules absorbed on the surface.

Figure 3(c) shows the map of silicon atoms on the samples. To note, there is one silicon atom per fluorosilane molecule, thus a Silicon map can be an indicator of how fluorosilane molecules are distributed on the surface of the sample. The yellow color shows regions where silicon atoms have high concentration while the dark color shows regions where the silicon atoms have low concentration. The occurrence of many spots with yellow color indicates that there is a wide coverage of fluorosilane molecules on the surface of the sample.

Figure 4 shows the infrared spectra of the zinc substrate, zinc substrate that underwent water-treatment, and zinc substrate that underwent water treatment technique as a pre-coating procedure before soaking in fluorosilane-ethanol solution. Meanwhile, Table 1 enumerates the assigned vibrational modes and wavenumbers of the peaks in Figure 4.

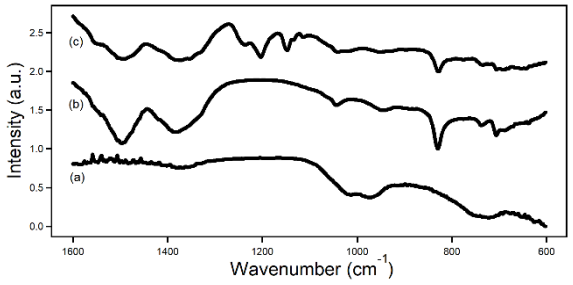


**Figure 4.** Infrared spectra of (a) zinc substrate, (b) zinc substrate that underwent water-treatment, and (c) zinc substrate that underwent water treatment technique as a pre-coating procedure before soaking in fluorosilane-ethanol solution.

Initially, the zinc substrate had peaks observed at 1049 $cm^{-1}$ and 1043 $cm^{-1}$ which may be due to the vibrational modes Zn–O–Zn stretching, and O–Zn–O–Zn stretching, respectively. The indicated vibrational modes show that the zinc substrate is already oxidized, as expected. Note that zinc is easily oxidizable thus expected to form zinc oxide at ambient condition.

Figure 5 might indicate the presence of a substantial amount of Zn-OH anchored on zinc oxide on the top layer of the zinc substrate after water treatment.The zinc substrate that underwent water-treatment shows vibrational peaks at 1497 $cm^{-1}$, 1385 $cm^{-1}$, 1042 $cm^{-1}$, 947 $cm^{-1}$, and 829 $cm^{-1}$. The said peaks were assigned to the vibrational modes Zn–OH bending, O–Zn–OH bending, Zn–O–Zn asymmetrical stretching, O–Zn–O–Zn asymmetrical stretching, and Zn–O bending, respectively.

Figure 6 shows the reaction of the fluorosilane molecules with water and its reaction to the water-treated zinc. This involved the reaction of the reactive tail of fluorosilane molecules with water molecules on the surface of the substrate (Figure 6(a)), which was followed by its attachment on the OH moieties on the zinc substrate as shown in Figure 6(b).

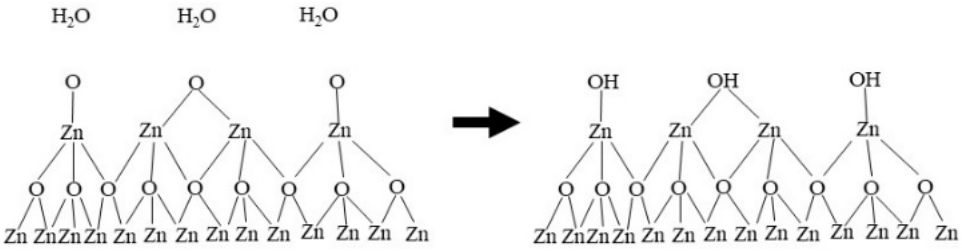


**Figure 5.** Zinc substrate after water treatment technique

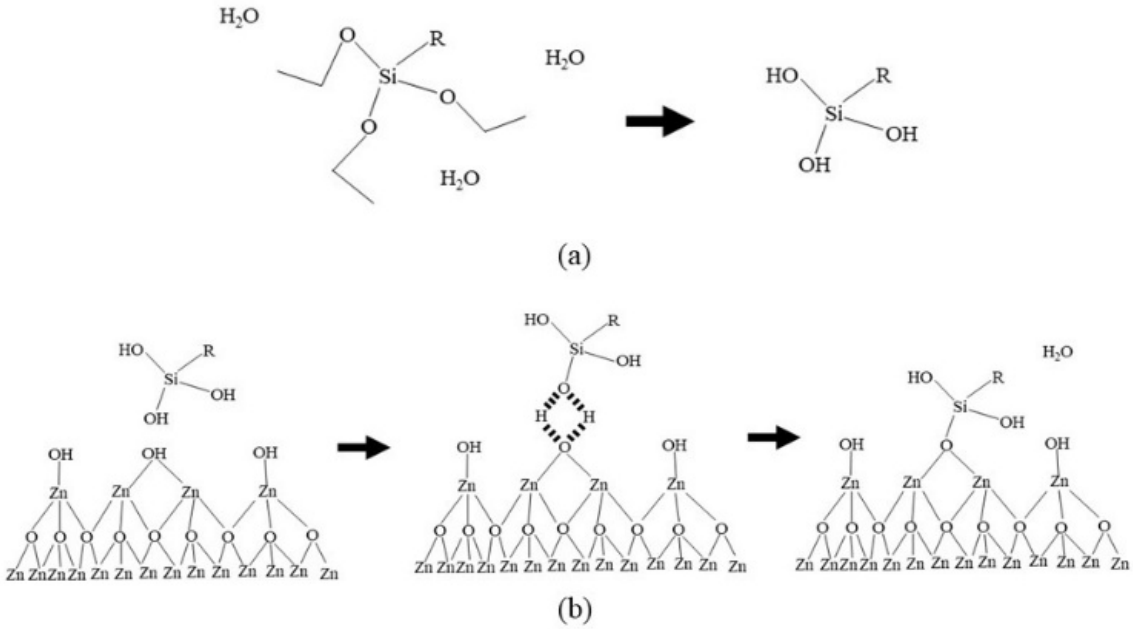


**Figure 6.** (a) Reaction of fluorosilane with water. (b) Probable grafting of fluorosilane molecules on water-treated zinc substrate. Note that R is the carbon-fluorine chain $C_{10}F_{17}$.

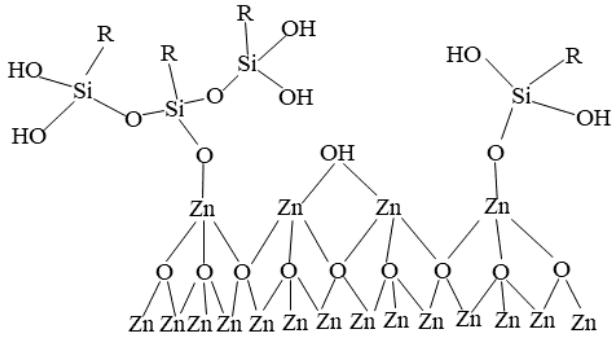


**Figure 7.** Water-treated Zinc substrate after soaking in fluorosilane-ethanol solution. Note that R is the carbon-fluorine chain $C_{10}F_{17}$.

Figure 7 shows a possible representation of the final configuration of the fluorosilane attached to the zinc substrate. The water treatment technique as a pre-coating procedure before soaking in fluorosilane-ethanol solution shows peaks at 1499 $cm^{-1}$, 1373 $cm^{-1}$, 1238 $cm^{-1}$, 1204 $cm^{-1}$, 1146 $cm^{-1}$, 1136 $cm^{-1}$, and 827 $cm^{-1}$. The presence of F–CF stretching, $F_2$–CF stretching, Si–O–Si asymmetrical stretching, O–Si–O–Si asymmetrical stretching, Si–O stretching might be attributed to the presence of fluorosilane molecules in the substrate. The coating of fluorosilane molecules on the water treated zinc substrate might be mediated by the reaction presented in Figure 6.

Water molecules introduced during the water pretreatment process may have two functions: (a) enhance the presence of OH moieties on the surface (Figure 5) and (b) creation of OH-terminated fluorosilane tails (Figure 6(a)); both of which are favorable in the grafting of fluorosilane molecules on the surface.

## 4. Conclusion

Zinc substrates with a superhydrophobic surface were successfully created through coating of fluorosilane molecules. Prior to the coating of fluorosilane molecules, the zinc substrate underwent a water-treatment technique at room temperature. The water contact angle of the samples went as high as $161.1° \pm 0.8°$. Water contact angles have lower values at lower fluorosilane-ethanol soaking times while they have higher values at higher soaking times. The optimum value of water contact angle was achieved at 240 min fluorosilane-ethanol soaking time. Mapping of the silicon atoms through Energy Dispersive Spectroscopy would infer that the fluorosilane molecules are widely distributed through the zinc substrate surface. After the water treatment process, Zn–OH vibration modes became apparent as shown in Infrared Spectroscopy. As such, the presence of Zn–OH was viewed as crucial in grafting of fluorosilane molecules since OH moieties react with hydrolyzed fluorosilane molecules to form chemical bonds. After the water-treated samples were soaked in fluorosilane-ethanol solution, vibration modes related to Si–O and C–F were detected. The said vibrational modes were attributed to the presence of grafted fluorosilane molecules.

Zinc metal with a superhydrophobic surface have advantages; they would have self-cleaning properties against dirt and have the ability to repel water molecules that could trigger further oxidation; these could potentially increase the market value of zinc metal. It is also advantageous that the treatment processes involve simple procedures that can be scaled up if mass production is eyed.

## Acknowledgements

The authors would like to acknowledge the University of the Philippines Los Baños Acceleration Growth through One Research and Extension in Action (UPLB AGORA) for funding the project.

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