

SIMPLE METHOD TO FABRICATE SUPERHYDROPHOBIC CARBON STEEL SURFACE

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Summary

This paper reported a simple method to fabricate superhydrophobic carbon steel surface. For this purpose, steel interfaces were coated by micro-nanostructured zinc. These textured surfaces were chemically treated using methyltrichlorosilane. The resulting surfaces were characterised using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), their wetting properties were investigated by static contact angle measurement. It was found that the steel surface displayed superhydrophobicity with water contact angle of $152^\circ \pm 2^\circ$ and low hysteresis.

Key words: Superhydrophobic, Zn electrodeposition, micro and nanostructures.

1. Introduction

Nature offers a large variety of examples of surfaces with amazing wettability properties, like the extreme water repellency, for instance of lotus leaves and butterfly wings. When a rain drop is put in contact with these surfaces, it rolls off and collects the dust particles with it at the same time, this is called a self-cleaning effect. These surfaces are the so-called superhydrophobic surfaces that have been deeply studied and well known, with water contact angle greater than 150° . Many studies demonstrate that these natural superhydrophobic surfaces own the micro and nanotexturation and the low wax-like material [1 - 5].

It is disputable that metal and alloyed materials are potentially used in both industry and life, however, these materials are susceptible to corrosion, particularly in the presence of electrolyte on the surface. As the superhydrophobic surfaces can repel water, the superhydrophobic metal or metal alloyed material surface can be ideal for anticorrosion application [6, 7]. Thus, in recent years, these solid artificial superhydrophobic surfaces have attracted significant attention in fundamental research and industrial fields. To mimic the natural superhydrophobic surface, nowadays, many methods have been developed to achieve the artificial metal superhydrophobic surface from various materials (Al, Cu, Fe, Zn, and stainless steel, etc) [8 - 12]. Overall, these surfaces are obtained through the combination of techniques for creation of surface roughness and low surface energy coating. The methods used for achieving

roughness on surface include bottom-up and top-down approaches, for instance, sol-gel methods, electroless deposition, wet etching, dry etching, chemical vapour deposition, pulsed laser deposition, and hydrothermal technique, etc. The low surface energy material coated on the rough surface commonly used the organic molecules including fluorinated molecules, derivative of silane molecules with $-\text{CH}_3$ or $-\text{CF}_3$ groups by different methods such as deposition technique, self-assembled monolayers [1 - 12].

In this paper, we focus on the fabrication of superhydrophobic steel surface via a simple method. A thin Zn layer was firstly deposited on the surface by facile electrodeposition with two electrodes and further functionalised with methyltrichlorosilane. These techniques are easy to handle and do not require highly-priced specific equipment. The resulting surfaces were characterised using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), their wetting properties were investigated by static contact angle measurement.

2. Material and method of experiment

2.1. Material

Methyltrichlorosilane, ethanol, acetone, H_2SO_4 , H_2O_2 , and $\text{Zn}(\text{CH}_3\text{COO})_2$ were obtained from Aldrich. The carbon steel X65 obtained from VINA Tan Phat company has the following surface composition: Fe (98.8%), C (0.12%), Mn (0.69%), Si (0.11%), Cr (0.02%), and Ni (0.01%), etc.

2.2. Preparation of superhydrophobic surface

The steel surfaces were cut to 0.1 x 1 x 0.5cm and used as substrates. These substrates were then polished by sand paper (100, 200, and 600) and subsequently degreased in acetone and ethanol, finally rinsed with distilled water.

The zinc deposition was synthesised on steel substrates by electrodeposition method. The two-electrode cells were used in which the cathode electrode was a steel substrate and the anode electrode was a Zn metal sheet (10 x 10mm). As an electrolyte, the mixture of 0.1M $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.1M NaCl solutions were dissolved in deionised water. A constant voltage of 1V was applied between two electrodes to grow Zn layer during 1,000 seconds. After electrolysis, the substrate was dried and annealed in a furnace at 250°C for 120 minutes.

The Zn coated steel substrates were UV/O₃ treated for 30 minutes to remove any organic contaminant and to generate surface hydroxyl -OH groups. The activated surface was further directly dipped into a solution containing 10wt% methyltrichlorosilane in ethanol for 12 hours. The resulting surface was rinsed in ethanol three times and then dried under a gentle nitrogen flow.

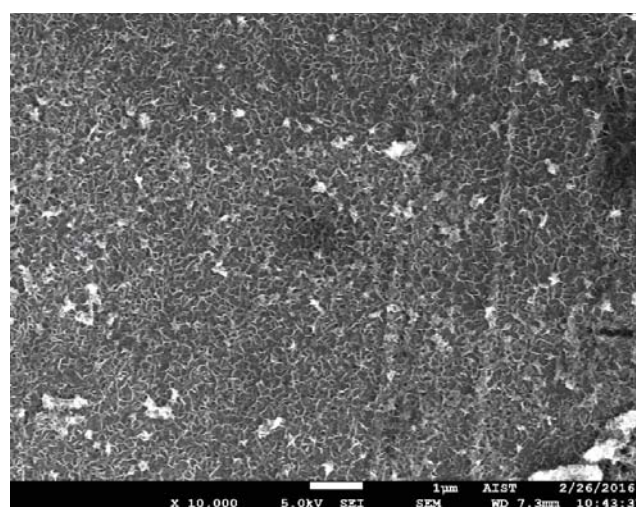
2.3. Surface analyses

Morphology and composition of the thin film were characterised by scanning electron microscope with X-ray microanalysis (SEM, JEOL 7600F with EDS, Oxford instruments). The wetting properties of all substrates were performed by measuring water static contact angle (CA) with OCA - data physics at three positions on each surface using 5 μL distilled water.

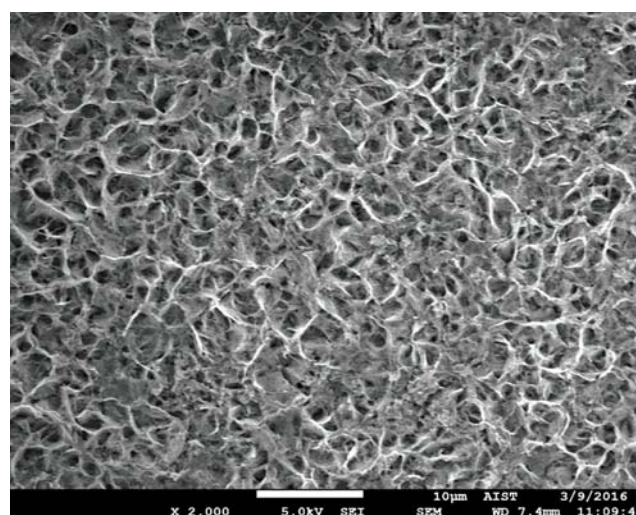
3. Results and discussion

3.1. Morphology and elemental composition

Figure 1 presents the SEM images and wettability of Zn coated steel substrates with 1,000 seconds of deposition. The thickness of Zn deposition on the surface was calculated by Alpha - Step U (KLA Tencor). Corresponding with 1,000 seconds of zinc deposition, the zinc thickness was 5.5 μm . It is apparent that the morphology of the coated substrate was changed with Zn deposition. In addition, the steel interface without zinc deposition had the same form structure with zinc coated interface and the zinc film was built on the wall of structure on steel interface, it is also noted that the obtained zinc structures were similar to the structure of pure zinc in the report of Brassard et al. [13]. It is evident that all surfaces had



(a) Steel surface



(b) Steel surface with 5.5 μm Zn

Figure 1. The SEM images: steel surface (a) and Zn coated steel surface with silanisation (b)

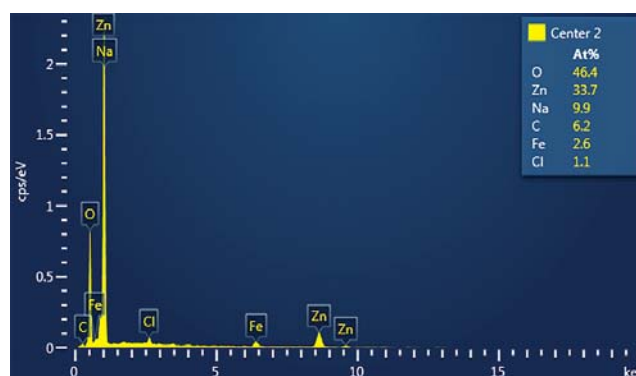


Figure 2. EDS analysis of the porous Zn-coated steel surface

several holes that increased the roughness interface. On the other hand, this was one of the two important factors that made the hydrophobic surface [14 - 19].

The composition of Zn thin coated on steel substrate was analysed by EDS as shown in Figure 2 which displayed the presence of zinc (8.6keV and 1.0keV). From the data, it is

apparent that thin Zn layers have been successfully introduced through the simple deposition method, in agreement with the published data [10].

The wettability of surface was performed by water contact angle (CA) measurement as shown in Figure 3. The steel interface without coating Zn and silane group ($\text{CH}_3\text{-Si}$) was hydrophilic with CA of $54^\circ \pm 2^\circ$, however, this steel surface became hydrophobic after silanisation with CA of $126^\circ \pm 2^\circ$, and superhydrophobic with water CA of $152^\circ \pm 2^\circ$ after coating of micro-nanostructured zinc and silanisation. Indeed, the steel surface was rough and did not contain any material owning low energy surface, resulting in the hydrophilic surface ($\text{CA} < 90^\circ$). After silane modification, CH_3 group which has a low energy surface was terminated on the steel surface, it leads to the hydrophobic steel substrate ($\text{CA} > 90^\circ$) [3, 4]. By micro-nanostructured zinc deposition on the steel surface, the rough surface was increased and the efficiency of silanisation reaction was improved, thus, the hydrophobic properties of the surface was dramatically enhanced, resulting in the superhydrophobic carbon steel surface with modification as shown in Figure 4a. Figure 4b presents the typical sequence of water droplet deposition on the sample, the information shows that it was

difficult to deposit a water droplet on this surface, in other words, the droplet was able to roll off the surface with a small sliding angle ($< 4^\circ$), it means that the surface had a low hysteresis with water.

4. Conclusions

We have successfully achieved the superhydrophobic steel surface via the simple method. By coating $5.5\mu\text{m}$ micro-nanostructured Zn layer and silanisation with methyltrichlorosilane, the carbon steel surface displays superhydrophobicity with water contact angle of $152^\circ \pm 2^\circ$ and low hysteresis. As the superhydrophobic surfaces can repel water, this superhydrophobic carbon steel surface could be ideal for anticorrosion application for the carbon steel pipeline.

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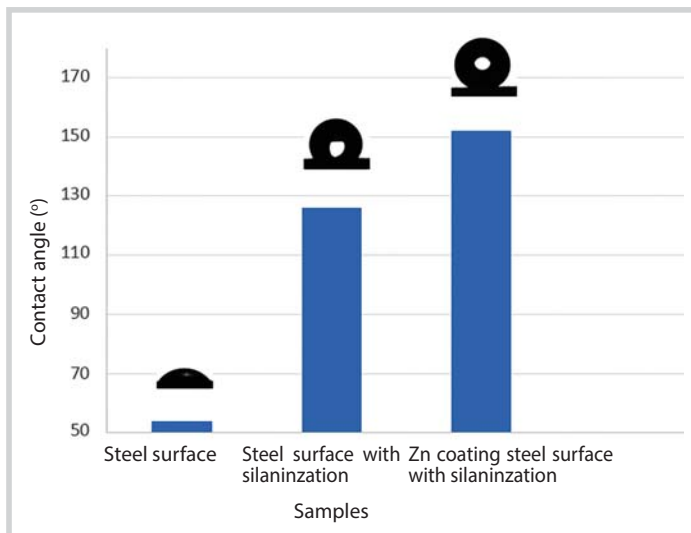


Figure 3. Wetting properties of substrate: steel substrate, steel substrate with silanisation, zinc coated steel substrate with silanisation

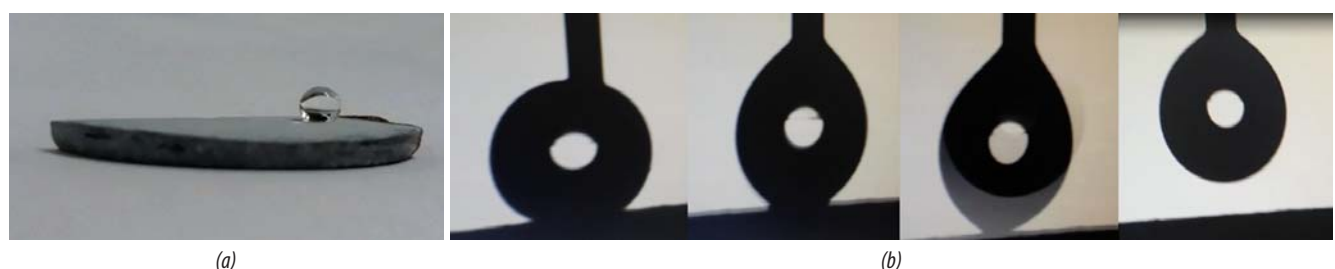


Figure 4. Wetting properties of substrate: steel substrate, steel substrate with silanisation, zinc coated steel substrate with silanisation

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