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OMNIPHOBIC CARBON STEEL SURFACE WITH GOOD WAX-REPELLENT PERFORMANCE

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Summary

In this report, superhydrophobic and omniphobic coatings were produced by a combination of creating a ZnO micro/nanostructure on the carbon steel surface and coating a low surface energy material. Before reducing the surface energy with 1H, 1H, 2H, 2H-perflu orodecyltriethoxysilane, the steel surface was electrodeposited by a micro/nanostructured ZnO layer for a controlled deposition time. The process resulted in the steel surfaces being superhydrophobic (contact angle of 165 ± 2°) and omniphobic with white oil, diesel oil (contact angle of 135 ± 2°) and paraffin (contact angle of 127 ± 2°). The properties of superhydrophobic/omniphobic steel surfaces were then fully analysed by SEM, XRD, FTIR and contact angle measurements.

Key words: Steel surface, superhydrophobic, omniphobic, paraffin, ZnO thin film, micro/nanostructure.

1. Introduction

The precipitation of waxes containing mainly paraffinic compounds is a serious problem in low-temperature crude oil production, such as reduced oil transportation efficiency, increased manufacturing cost, even causing pipelines to be blocked, etc. [1, 2]. To predict wax deposition, there are various methods based on two main ways of adding additives and using appropriate pipeline surface materials. Additives are categorised into different kinds depending on its activating mechanism: anti-sticking agents, dispersants, or inhibitors. Among them, adding additives is mostly used because of its effectiveness in preventing the wax precipitation, however it is costly and not environmentally friendly [3]. Therefore, in recent years, many research groups have made great efforts on pipeline surface materials, especially focusing on wax-repellent coatings for pipelines [4, 5].

In fact, the fabrication of wax-repellent surfaces is a kind of making liquid-repellent surfaces. It is based on the wetting property of the surface, which is determined by a contact angle (CA) between the liquid and the solid surface. The value of contact angle depends on the characteristics of the surface (such as composition, chemical finishing, roughness, etc.) and the interfacial surface tension (solid - liquid - vapor) [6 - 8].

When a liquid droplet is deposited on a perfected smooth and chemical homogeneous surface, the contact angle is derived from Young's equation (θ) [9 - 11]:

$$Cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

where γ refers to the interfacial tension; S, L, and V refer to the solid, liquid and vapor phases, respectively. Based on the water contact angle, a surface can be classified as superhydrophilic if the contact angle ≈ 0, hydrophilic if the contact angle is less than 90°, hydrophobic if the contact angle is greater than 90°. Note that the maximum water contact angle on "a perfected smooth and chemical homogeneous surface" is about 130° [8]. Similar to water, based on the contact angle of liquid having a low surface tension (such as oil, alcohol, or another organic solvent), the surface can be categorised as superomniphilic, ominiphilic and omniphobic [6, 10].

In fact, the surface always illustrates both physical defects (or roughness) and chemical inhomogeneity. In this case, the contact angle between the liquid and the

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surface is defined as the apparent contact angle that has a strong bond with the contact angle by Young's equation (as described in "wetting on rough surfaces - the Cassie-Baxter state and the Wenzel state).

According to some reports [8, 12, 13], the fabrication of liquid-repellent surfaces has been studied based on creating a re-entrant structure or a combination between textured surface and chemically modified surface. The textured surface increases the surface roughness while the chemical modification of the surface leads to a decrease in the surface energy [14, 15].

To create the textured surface, there are several methods such as sandblasting, particle coating, plasma treatment, chemical treatment, lithography, deep coating, and vapor deposition. However, it may be noted that the large-scale commercial applications of these techniques are limited due to the required special equipment, expensive material, complex and long fabrication process [4].

Chemically, there are two main methods for surface treatment: the first one is the deposition of hydrophobic material (via physisorption) such as fluorocarbon polymer, teflon or cytop by spin coating, plasma coating, etc. The other way is the covalent immobilisation of a low surface energy via chemisorption: silanisation for oxide surfaces, thiol alkylation for noble metal surfaces [6].

In recent years, a few omniphobic and superhydrophobic steel surfaces have been fabricated [16], but they are mesh steel surfaces and have not been wax-tested yet [2, 3, 5,17]. In this article, we introduce a simple process to fabricate wax-repellent steel surfaces. First, the steel substrate is polished by sandpaper, then it is coated with a micro/nanostructured ZnO layer. Finally, this surface is modified with fluoro substance. The preparation of wax-repellent steel surface is analysed by Scanning Electron Microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and contact angle measurements for water, oil liquid, diesel, and paraffin.

2. Experimental

2.1. Materials

Methyltrichlorosilane, ethanol, acetone, H_2SO_4, H_2O_2, NH_3, and $Zn(CH_3COO)_2$ and white oil are obtained from Sigma-Aldrich. In this study, CT3 steel substrate is bought from China and consists of Fe (42.89%), C (0.14%), Mn (11.12%), Si (0.13%), Cr (0.02%), and Zn (0.51%). Paraffin wax is from China and crude oil is from Vietnam (Bach Ho crude).

2.2. Preparation of superhydrophobic steel surface

2.2.1. Formation of micro/nanostructured ZnO coating

The steel surfaces are cut into 1.5 cm × 3.0 cm × 3.0 cm for the CT3. The substrates are then polished by sandpaper (100, 200, and 600 grit) and subsequently degreased in acetone and ethanol, and finally rinsed with distilled water.

The steel substrate is firstly dipped into 0.1 M HCl solution for 30 seconds before the zinc electrodeposition process is conducted for different time durations: 5 minutes, 15 minutes, 30 minutes, 45 minutes, and 60 minutes. More details concerning this process are described in our previous article [10, 18].

A 2-electrode cell is used, in which cathode is the steel substrate, anode is a Zn metal sheet (0.2 cm × 2 cm × 5 cm) and the electrolyte is deionised water. A constant voltage of 1 V is applied between the two electrodes to grow the Zn layer for different durations. After electrolysis, the substrate is cleaned with deionised water and then dried. Finally, the substrate is annealed in a furnace at 250^{o}C for 120 minutes to form a ZnO thin film coating on the steel surface.

2.2.2. Surface functionalisation by silanisation

The ZnO-coated steel substrates are UV/O3 treated for 30 minutes to remove any organic contaminants and to generate surface hydroxyl -OH groups. The activated surface is then directly dipped into a 50 mL hexane containing 50 microliters 1H, 1H, 2H, 2H-perfluorodecyltri ethoxysilane. The substrate is rinsed 3 times with hexane, 3 times with ethanol, and then dried under a gentle nitrogen flow.

Morphology and composition of the thin film is checked by JEOL JSM-7600F SEM and an Oxford Instruments EDS X-ray microanalyser.

The chemical surface is analysed by FTIR, XRD and EDX while the wetting properties of all substrates are determined by measuring static contact angle of water, white oil, diesel and melting paraffin with OCA - DataPhysics Instruments at 3 positions on each surface using 5 μl distilled water or oil.

3. Results and discussion

3.1. SEM observation

To consider the effect of structure on superhydrophobic and omniphobic properties, in this study, the steel substrate is coated a micro/nanostructured ZnO layer by electrodeposition using acetate zinc solution for various time durations: 5, 15, 30, 45 and 60 minutes. All these surfaces then are treated with 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane.

Figure 1 shows SEM images of steel substrate before and after ZnO coating by electrodeposition method: (a) steel substrate without ZnO coating (M_0), (b) steel substrate with ZnO electrodeposition for 5 minutes (M_1), (c) steel substrate with ZnO electrodeposition for 15 minutes (M_2), (d) steel substrate with ZnO electrodeposition for 30 minutes (M_3), (e) steel substrate with ZnO electrodeposition for 45 minutes (M_4) and (f) steel substrate with ZnO electrodeposition for 60 minutes (M_5).

The cathodic electrochemical deposition reactions to grow the nano/

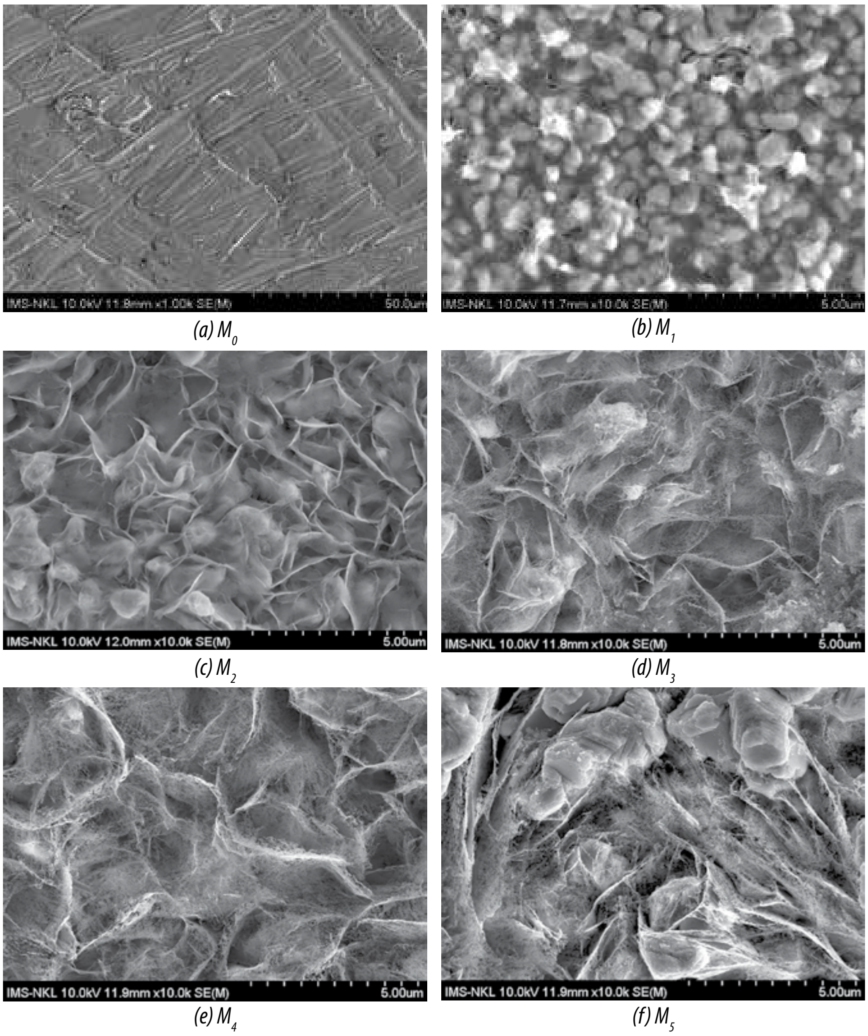


Figure 1. *SEM images: (a) steel substrate without ZnO coating (M_0), (b) steel substrate with ZnO electrodeposition for 5 minutes (M_1), (c) steel substrate with ZnO electrodeposition for 15 minutes (M_2), (d) steel substrate with ZnO electrodeposition for 30 minutes (M_3), (e) steel substrate with ZnO electrodeposition for 45 minutes (M_4) and (f) steel substrate with ZnO electrodeposition for 60 minutes (M_5).*

microstructure ZnO layer are proposed as follows [19].

$$O_2 + 2H_2O + 4e- \rightarrow 4OH^- \quad (1)$$

$$Zn^{2+} + xOH^- \leftrightarrow Zn(OH)_x^{2-x} \quad (2)$$

$$Zn(OH)_x^{2-x} \leftrightarrow ZnO + H_2O + (x-2)OH^- \quad (3)$$

First, OH^- ions are generated on the substrate by reducing O_2 precursor (reaction 1). Secondly, Zn^{2+} ions and OH^- are combined to generate $Zn(OH)_x^{2-x}$ ions (reaction 2). Finally, ZnO is formed by dehydration of $Zn(OH)_x^{2-x}$ ions (reaction 3).

As shown in Figure 1a, the ZnO-uncoated surface of CTs-1 is rough with some minor scratches, holes, and other defects. However, after a 5-minute electrodeposition, the ZnO particles having diameters of about 500 nm appear on the substrate (Figure 1b). The deposition time lasting more than 15 minutes results in the formation of a pattern with flower shapes, each with a spherical particle inside, which increases the roughness of the surface.

3.2. XRD analysis

Figure 2 presents the X-ray diffraction (XRD) pattern of steel substrate and of micro/nanostructured ZnO-coated steel substrate. The peak in the XRD spectra in Figure 3 can belong to the (100), (002), (101), (110), (112), and (201) crystallographic planes of wurtzite hexagonal ZnO crystal structure. The diffraction pattern indicates pure crystallinity of ZnO micro/nanostructure.

3.3. EDX analysis

The chemical compositions of steel surfaces without and with ZnO coating are also measured by energy-dispersion X-ray (EDX spectroscopy) as shown in Figure 3.

From Figure 3, before coating with the ZnO layer, the steel surface mostly contains C and Fe atoms with proportions of 30.1% and 69.2%, respectively. Meanwhile, the ZnO-coated steel surface presents a high amount of Zn and O atoms with 33.7 and 46.4%, respectively.

From those results, it might confirm that the micro/nanostructured ZnO layer has been coated on the steel surface by electrodeposition method.

3.4. Effect of micro/nanostructured ZnO coating to the superhydrophobicity and omniphobicity of the steel surface

In this section, four liquids (water, white oil, diesel oil and paraffin) are used to test the superhydrophobic/omniphobic properties of the steel surfaces. For each liquid, the contact angles (CA) on steel surface and micro/nanostructured ZnO coated-steel surface are measured and plotted in Figure 4.

On the steel surface without ZnO coating (M_0), the surface is hydrophobic (contact angle = 126°), omniphilic with white oil (contact angle = 78°, total spreading diesel and paraffin). When a steel surface is deposited with ZnO nanoparticles (M_1), it becomes superomniphobic for all oils (contact angle = 0) and less hydrophobic (contact angle = 110°). Although the surface M_0 is less rough than M_1 and has omniphilic properties with contact angle < 90°, the surface M_1 is more omniphilic and water easily enters among the particles at Wenzel state.

For other surfaces (M_2, M_3, M_4 and M_5) that are electrodeposited longer, their roughness increases dramatically, resulting in these surfaces being superhydrophobic with a contact angle of more than 160° and omniphobic (contact angle > 110°). Particularly, the surfaces M_4 and M_5 having the electrodeposition time of more than 45 minutes are the highest omniphobic; the contact angle value of white oil, diesel and paraffin are around 130°.

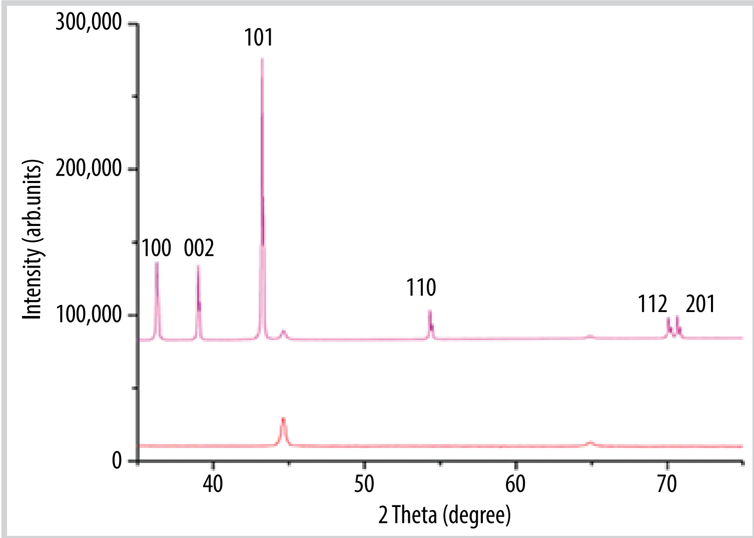
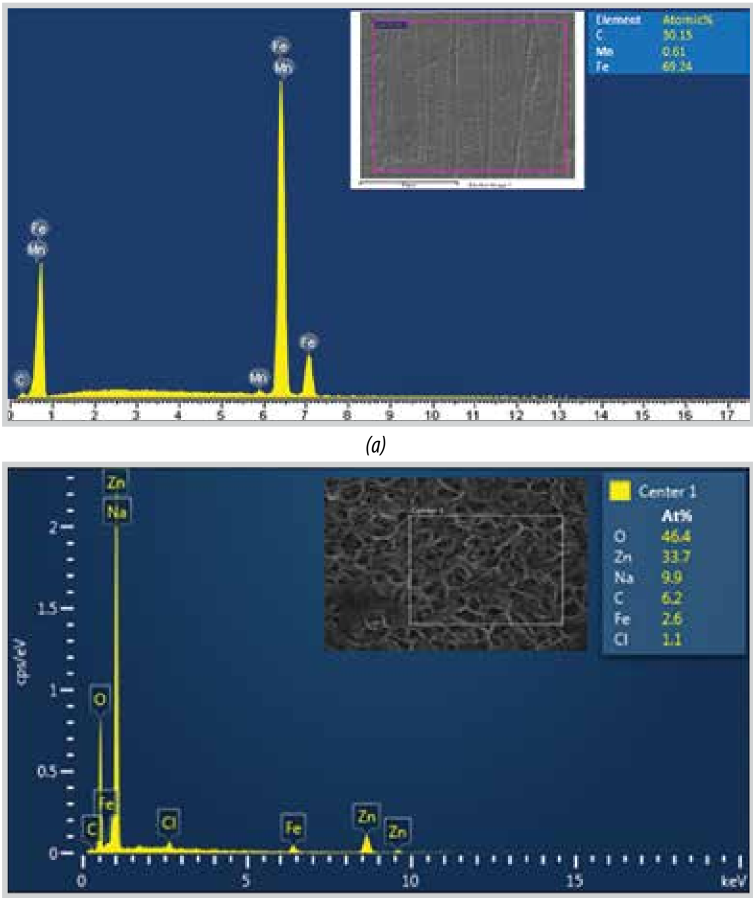


Figure 2. *X-ray diffraction spectra of steel substrate without ZnO coating (orange line), and micro/nanostructured ZnO-coated steel substrate (purple line).*



(a)

(b)

Figure 3. *EDX spectroscopy of steel surface without ZnO coating (a) and with ZnO coating (b).*

3.5. Effect of time chemical reactions on superhydrophobicity and omniphobicity of the micro/nanostructured ZnO-coated steel surface

In this section, time silanization reactions between 1H,1H, 2H, 2H-perfluorodecyltriethoxysilane and micro/nanostructured ZnO-

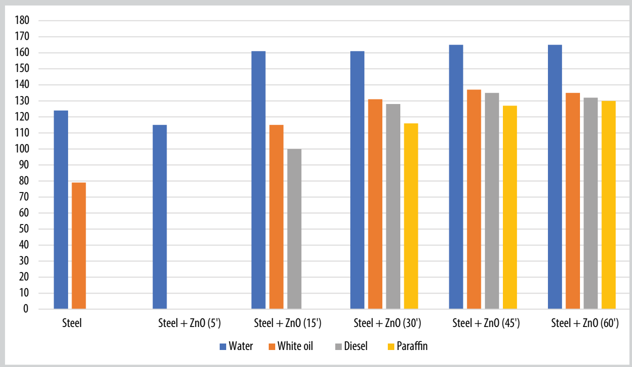


***Figure 4.** Contact angle of water, white oil, diesel and paraffin on steel surface and different ZnO-coated steel surface.*

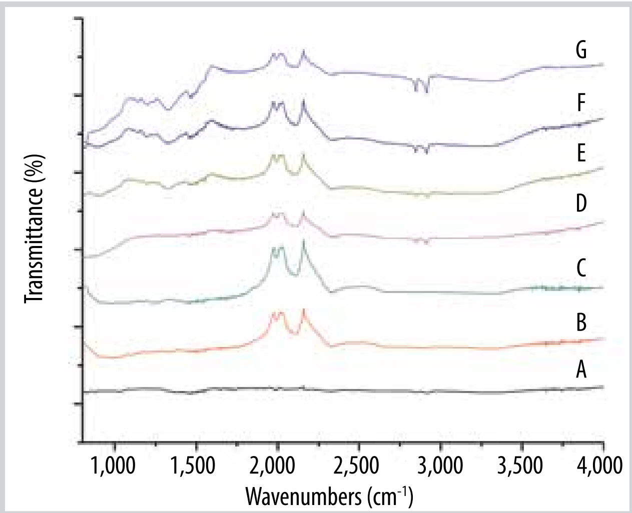


***Figure 5.** FTIR spectra of the as-prepared steel surface (curve A), ZnO-coated steel surface (B), ZnO-coated surface are modified with silane for 0.5 hours (C), 1 hour (D), 2 hours (E), 6 hours (F), and 16 hours (G).*

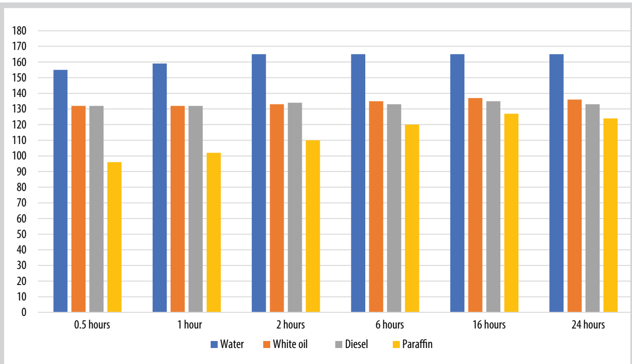


***Figure 6.** Contact angle of water, white oil, diesel and paraffin on ZnO-coated steel surface with silanisation treatment.*

coated steel surface are investigated to show how it affects the wettability of substrate. In fact, the surface M4 (with 45 minutes of ZnO electrodeposition) reacts with that silane for various time durations: 0.5 hours, 1 hour, 2 hours, 6 hours , and 16 hours.

From Figure 5, the FTIR spectrum of steel sample (line A) does not show any functional group pick. When the steel surface is coated with a micro/nanostructured ZnO layer, two picks at 1,993 cm^{-1} and 2,110 cm^{-1} appear and relate to ZnO stretching. Further, this surface is modified with silane, the intensity of picks at 1,993 cm^{-1} and 2110 cm^{-1} decreases, and two picks appear at 2,847 cm^{-1} and 2,914 cm^{-1}, which correspond to the $C\text{-}H_x$ stretching modes and have density increasing with the reaction time. If the silanisation reaction takes place for 0.5 hours, the pick of $C\text{-}H_x$ stretching modes still does not appear, however, it occurs after a one-hour reaction.

In this section, the contact angle of the four above-mentioned liquids is also measured (Figure 6). It is obvious that all samples become superhydrophobic (contact angle > 150°) and omniphobic after 0.5 hours of chemical treatment. However, the contact angle values of four liquids are stable after 6 hours of silanisation treatment (with contact angle of water about 160°, contact angle of oil about 135° and contact angle of paraffin about 128°).

4. Conclusion

In this project, we have successfully studied superhydrophobic and omniphobic steel surfaces. A simple electrodeposition method has generated micro/nanostructured ZnO layer coating on the steel surface. From the SEM analysis, it shows that different electrodeposition times produced different ZnO layer structures. In addition, the results by EDX and XRD also illustrated that the micro/nanostructured ZnO layer was crystal. The modification with 1H, 1H, 2H, 2H-perfluoro decyltriethoxysilane for 6 hours gave the best results in terms of static contact angle with the values of 160 ± 2° and 130 ± 2° for water and oil, respectively. However, this result has presented good wax-repellent properties.

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