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Facile approach for omniphobic and anti-icing on Fe surface

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Abstract. *The functionalized process refers to a new concept, which aims to modify the physical and chemical properties of the original surface for specific purposes.. The various applications might be named liquid repellent, anti-icing, anti-reflection, water harvesting, anti-biofouling, etc. This study proposes a simple and fast fabrication method based on etching incorporated with low surface energy chemical compound coating to functionalize the Iron (Fe) surface for omniphobic and anti-icing characteristics. After being functionalized, the surface reveals an omniphobic state with various liquids and extremely low adhesion to ice bulk. The research might suggest solutions for manufacturing functional surfaces oriented to outdoor applications such as windshields, rearview mirrors, anti-fouling surfaces, etc.*

Keywords: Omniphobic; Fe; anti-icing.
Classification numbers: 68.35.Np.

1. Introduction

Functional surfaces allow us to modify the surface of a material to maintain the desired functions from external agents, avoid the deposition of substances, improve the properties' efficiency, or achieve new functions that could not be found on the original materials [1–4]. The applications of functional surfaces are extremely wide owing to the ease of texturing process and advanced techniques. Among them, innovative properties such as anti-icing [5–11], anti-reflective [12–14] and water harvesting [15] have been discussed and reported by many scientists due to their topicality and urgency. Surface treatment approaches have also been documented consisting of directly texturing on the substrate or developing the coating material, facilitating the transition from laboratory to industrial fabrication. The application of different techniques to achieve different properties depends on the intended use.

Omniphobic state refers to the state in which the surface is extremely difficult to be wetted by the liquid. Therefore, the contact angle at the three-phase contact line often exceeds 150 degrees. The omniphobic surface has been inspired by the non-wetting behavior of the lotus leaf, which is facilitated by the unique micro-nano structure at the leaf surface [16]. Fig. 1a depicts the close view of a lotus leaf structure using the SEM (Scanning Electron Microscopy) method. As shown in the figure, the cylindrical nanometer ($\sim$ 100 nm) structures are surrounded by a waxy layer similar to candle wax, which is the original liquid non-adherent material. In addition, such structures can also be found in some penguins' feather structures [17]. Thanks to the multi-layered micro-nano feathers and characteristic oil layer, water cannot penetrate the air between the structures, allowing the penguins to accelerate quickly when they need to jump out of the water and land on higher ground [18]. Fig. 1b presents a simulated surface fabricated by ion etching combined with a coating of hydrophobic chemical compounds. Such artificial textured surfaces also exhibit extremely high water-repellent properties which might be compared to the lotus leaf. Owing to the innovative application, omniphobic surfaces have been focused on research and fabrication in the last decade and recently present a comparable effect with natural surfaces, which might even propose a higher performance in terms of contact angle and liquid mobility. As mentioned, the fabrication of omniphobic surfaces required tight control over the size and morphology of surface structures.

The technique is also used to develop transparent hydrophobic surfaces such as car windshields and self-cleaning windows [16, 19, 20]. By coating a monolayer of silica nanoparticles and following by DREI etching routine, it is possible to generate a transparent and completely non-wetting surface with contact angles close to 170° and transmittance higher than 94%. On the other hand, texture surfaces with engineered veins have been found in laboratory microfluidic devices and significantly improve surface-based bioanalysis [2, 21]. In addition, the examination of hydrophobic paper with unique properties has been considered for applications in the electronics and medical industries. Hydrophobic paper is synthesized in a free organic environment and is environmentally friendly. Furthermore, its non-wetting property regarding water and organic solvents will be an ideal basis for the development of sensors and electronic chips to detect substances and skin analysis. The recent development of hydrophobic materials has been named in the micro fuel cell chips. The reactions in the fuel cell that produce Co_2 will be able to escape through hydrophobic membranes consisting of many small vents, while its hydrophobic properties will prevent liquid fuel from leaking through. In addition, the prominent application of non-wetting can be illustrated in heat exchangers, where they always give a separate condensate state instead of condensing in layers and inhibiting heat exchange. This proposes a great potential application for generators, heating and air conditioning systems and desalination.

Recent studies have demonstrated that superhydrophobic surfaces can eliminate or prevent the accumulation of snow and ice on the surfaces [5–11, 23–27]. This proposes a very urgent solution because ice formation on surfaces near the earth's surface is inevitable due to the rapid coalescence of condensed water droplets. Ice accumulation increases the area and strong adhesion, making it difficult to remove from the surface, causing a lot of inconvenience and obstacles to human life, industry and transportation. From the physical point of view, snow and ice are formed under the high humidity environment at cold temperatures (below 0°C). Among the reported solutions, the superhydrophobic surface has been believed as the most viable candidate owing to its valuable properties including an extremely high liquid contact angle (normally higher than 150

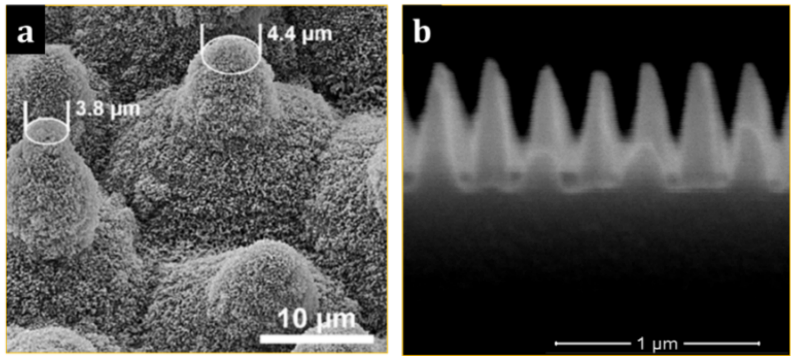

Fig. 1. Lotus leaf (a) [22] and mimicked surface fabricated by the author (b).

degrees) and a very low sliding angle (normally lower than 2 degrees). The sliding angle corresponds to the tilted angle at which the water droplet starts to depart from the surface. This leads to the liquid coming into contact with the surface will have very high mobility, easily rolling off the surface before it can solidify, or, in the case of ice already formed, it will be easily removed due to the low surface contact area. Among the methods of superhydrophobic preparation, the two-level structure demonstrates high efficiency in the prevention and removal of ice and snow. Such a two-level structure refers to the micro and nanostructure simultaneously present on a surface, in which the nano-size structures (nano hairs, nanotubes, nanopillars) are generated on the body of micro-size features. This structure after functionalized with low surface energy chemical illustrates the outstanding hydrophobicity. This might be explained by the advantages of the micro-nano level that can prevent the penetration of water between structures, which profoundly raises the energy barrier in the transition from Cassie-Baxter to Wenzel state.

In this study, we introduce a simple and facile process to fabricate non-wetting and anti-icing surfaces on the Fe substrate by using the etching method incorporated with a self-assembly-coating process of the low-energy chemical compound. The hydrophobia of the functional surface was examined quantitatively by pouring the water for 15 minutes, while the anti-icing in terms of adhesion strength was evaluated by a sensitive force sensor. The results exhibit the outstanding performance of superhydrophobic surfaces in comparison with other surfaces and illustrate the potential solution for functional surfaces working outdoors such as windshields, rearview mirrors, or vehicle bodywork.

2. Experiment

Figure 2 depicts the process of fabricating an omniphobic surface on the Fe substrate. The two-level structure was fabricated by the wet etching method using an acid solution. Hydrochloric acid (HCl) solution will be mixed with Propanol-2 and deionized water in a 10:1:20 ratio to prepare the etching solution. Fe plate (length x width x thickness are 3 cm x 3 cm x 0.1 cm) was immersed in the solution for 30 minutes to ensure a slow etching rate. After etching, the rough sample was cleaned rapidly with deionized water 3 times and dried with nitrogen gas. The fabricated sample surface shows filamentous nanostructures with a regular height of about 40 nm on the Fe substrate.

After drying, the vapor deposition method brought the sample to the coating process with a low surface energy chemical compound. The sample was placed in a closed box with the presence of a FOTS (1H,1H,2H,2H-Perfluorooctyltriethoxysilane) solution to ensure a monolayer of low surface energy compound attached to the surface structure [24,28,29] . FOTS (C14H19F13O3Si) is a fluorine-based polymer that is majorly used for improving the wettability of the substrate by controlling the surface energy. It facilitates a superhydrophobic coating by enriching the surface with a -CF3 group (expose to the wetting environment) with a water contact angle above 150° while the other end linked with the coated surface through Si-O- bonding. The wettability of the sample was evaluated by a contact angle measuring device (Kyowa Co., Ltd, Japan). The higher the contact angle, the lower the wettability of the sample and vice versa. The contact angle measurement was calculated at least 5 times at different positions and took the average. SEM (Scanning Electron Microscopy) was used to investigate the surface morphology.

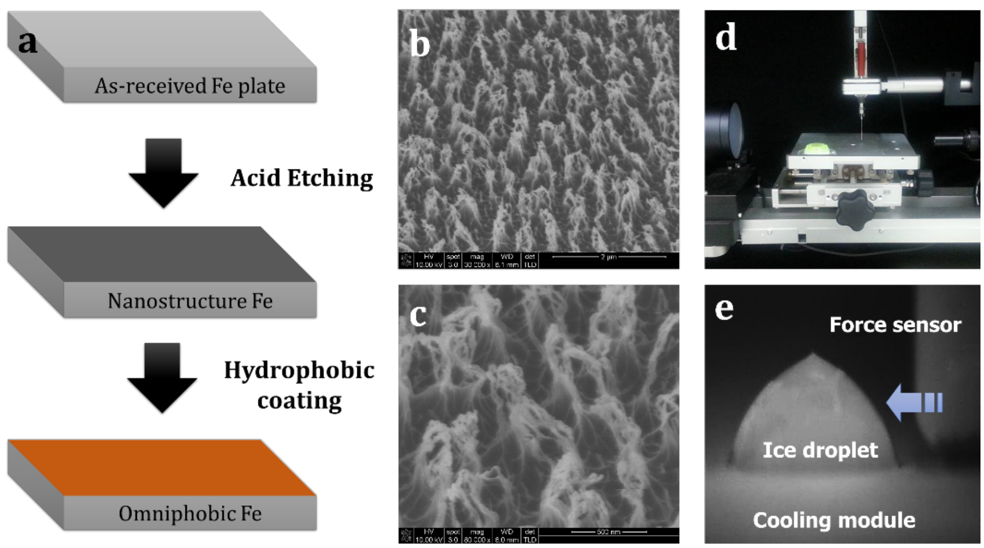

Fig. 2. The fabrication process of omniphobic surface (a), SEM images of nanostructure surface after etching (b, c), contact angle measurement (d) and ice-adhesion measurement setup (e).

The anti-icing performance of fabricated surfaces was investigated by measuring the adhesion strength at the interface (Fig. 2e). A small volume of a water droplet was tenderly dropped on the surface before freezing. After solidification, a force sensor was used to apply on the ice bulk and push horizontally until it was detached from the surface. The force extracted from the collision was collected and analyzed by computer software to figure out the exact adhesion strength between ice and substrate.

3. Results and discussion

Figure 2(c) presents the morphology of the Fe plate after etching. A uniform array of fibrous nanostructures with a height of about 40 nm was generated on the surface as the result of the chemical reaction with the acid solution. Such a rough structure after being coated with a hydrophobic chemical layer of FOTS presented a completely non-wetting surface with a spherical-like shape with a very high water contact angle (higher than 160°), whereas on the as-received plate (bare Fe), the contact angle was only about 90° (Table 1).

This might be explained by the Cassie-Baxter state at the liquid-solid-air interface, where water droplets only stayed on the top of nanofibers instead of deep penetration in the surface structure. Due to the very small size and water-repellent properties, the radius of the meniscus formed by water between the two neighboring nanopillars has a very large radius, hence the pressure $P = 2\gamma/R$ (γ is the water surface tension) which directs from the inside to the outside of the water droplet is trivial, meaning that the transition is very unlikely. These results illustrate the importance of the combination of nanostructure with chemical compounds in determining the liquid formation at the interface. Without the chemical compound, the surface resulted in a high wetting state (superhydrophilic/ultra hydrophilic) state with a contact angle of fewer than 20 degrees. The high contact angle and mobility of liquid droplets also can be observed when dealing with hexadecane and silicon oil (Table 1). Liquid droplets were found easily depart from the surface as the sliding angle are quite low (1,2,2 degrees for water, silicon oil and hexadecane, respectively), demonstrating the omniphobic properties of fabricated Fe substrate.

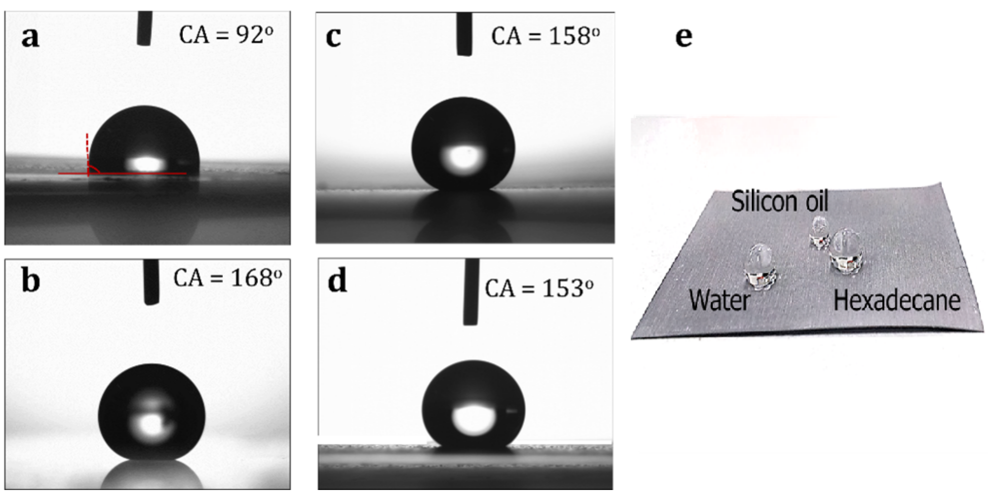

Fig. 3. The water contact angle on as-received Fe (a) and omniphobic Fe surface (b), silicon oil (c) and hexadecane (d) contact angle on omniphobic Fe and real-time droplets on omniphobic Fe surface (e).

To investigate the self-cleaning ability for applications-oriented, the water-repellent test was carried on by spraying water on a functionalized Fe surface. We prepared fine sand arranged in different thicknesses to simulate the actual dusted surface. Fig. 4 shows the very high water repellency performance of the omniphobic Fe surface when the water completely removed all the impurities in its path. The functional surface was tested at least 50 times and demonstrated high repeatability, showing potential for applications (Fig. 4).

Figure 5 depicted the adhesion measurement of ice on surfaces with different conditions after 30 times experiments and averaged. The highest value belonged to the NF (Nanostructure Fe) sample when it exceeds 869 KPa and can be explained by the uniformity of surface roughness.

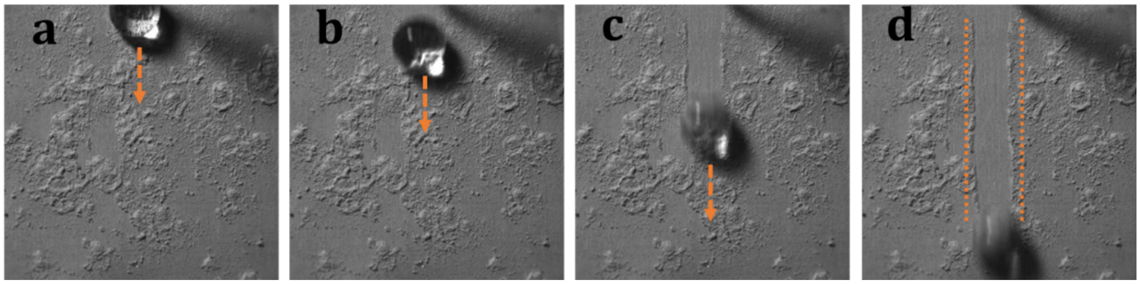

Fig. 4. Self-cleaning efficiency on functionalized Fe surface. Images a, b, c and d correspond to the process of a water droplet being dropped and removing all dust in its path.

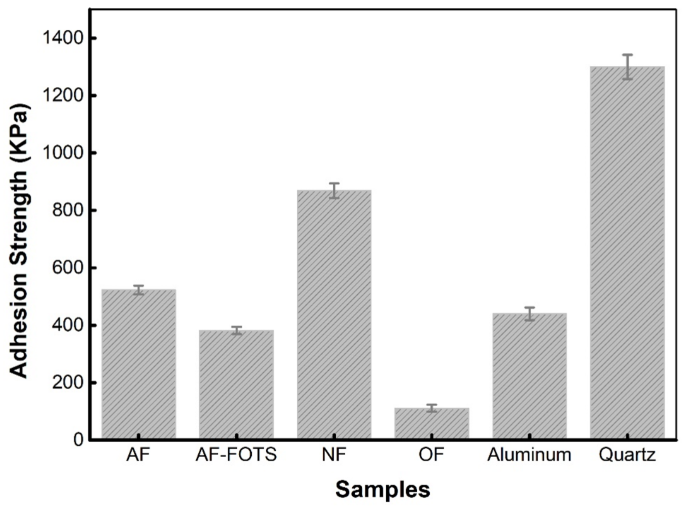

Fig. 5. Adhesion strength measurement on different surfaces (using water).

Water droplets were found easily to penetrate the nanostructure before freezing, illustrating an "anchoring" effect and leading to extreme difficulty in removing ice drops. On the other hand, the AF (As-received Fe) sample introduced a smooth surface and resulted in low adhesion strength even though it lacked a chemical coating layer. This can be explained by the dominance of contact area between ice and surface when it was proportional to the adhesion strength. The lowest value was found on the omniphobic Fe surface when it exhibited quite low adhesion strength compared to other Fe-based surfaces and reference surfaces. The ice-surface adhesion was about 111 KPa, which corresponded to 5 times and 8 times lower than AF and NF surfaces, respectively, demonstrating the dramatic reduction in ice-surface interaction. This might be explained by the Cassie-Baxter state of the water droplet during the whole solidified time, which resulted in a very low contact area formation. Ice bulk therefore can be detached easily from the interface. The experiment results revealed the importance of the combination of surface roughness and hydrophobic compound. The optimized condition exhibited the advantage in the anti-icing aspect in terms of adhesion strength and proposed the potential for practical applications.

Table 1. Measurements of investigated samples

Name	Contact angle (degree)			Sliding angle (degree)			Adhesion strength
	Water oil	Silicon	Hexadecane	Water oil	Silicon	Hexadecane (KPa)	
As-received Fe (AF)	67	68	60	21	20	20	523 ± 15
AF coated FOTS	86	88	58	14	11	10	382 ± 13
Nanostructure Fe (NF)	22	20	19	--	--	--	869 ± 25
Omniphobic Fe (OF)	162	158	153	1	2	2	111 ± 12
Aluminum (reference)	87	45	42	22	27	29	440 ± 22
Quartz Glass (reference)	117	55	50	19	26	24	1300 ± 42

"–": cannot find the sliding of liquid

4. Conclusion

In this study, a simple and fast fabrication method has been presented for the omniphobic functional surface fabricated on the Fe substrate. The appropriate combination of surface roughness and hydrophobic chemical compound documented a completely liquid-repellent state with several types of examined liquids when removing all contaminants in the droplet's path. The practical potential in anti-icing of the functional surface was tested and demonstrated the extreme reduction in adhesion strength compared to references and other Fe-based samples. The research results have proposed a facile fabrication process of functional surfaces which shows the high potential for practical applications working outdoors including windshields, device's shells, or vehicle's bodywork.

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Conflict of interest

The authors declare that they have no competing financial interests.

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