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Original Article

Surface wettability controlling for self-cleaning and anti-adhesive purposes

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ABSTRACT

The study proposes a method of surface fabrication inspired by the water self-cleaning phenomenon of lotus leaf, penguin feather, and rice leaf. The unique combination of micro and nanostructure impedes water penetration through textures. The micro and nanostructure have been generated using a wet etching by hydrochloric incorporated with an additional wet etching using hydrofluoric acid. These super hydrophilic regions will be functionalized using low-energy chemical compounds to enhance the water repellency and water-driven ability. After the coating process, the investigation demonstrates an outstanding self-cleaning effect and extremely low friction between liquid and functional surfaces. Interestingly, these surfaces might support a water-bouncing effect, which cannot be found on natural surfaces. After the collision, the water droplet spreads the volume, bounces back into the air, and does not leave any wetting traces on the surface. This can be explained by the high hydrophobicity, which is facilitated by the energy reduction generated after the coating step. The results illustrate the potential of functional surfaces for application-oriented self-cleaning, anti-adhesion, and water harvesting purposes as well.

Keywords: Jumping water, nanostructure, self-cleaning, surface wettability, water collection

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INTRODUCTION

Functional surfaces are a concept that refers to surfaces that are processed to simulate natural morphology oriented for specific applications. Open and optimized research is focused on and achievements are achieved thanks to the development of manufacturing technologies.

The applications that surface functionalization targets are very wide, including prominent areas such as anti-fouling (self-cleaning),[1,2] anti-wet (liquid repellency),[3-5] snow and ice resistance,[6] or water collection.[7,8] Among those ideas, the non-wet surface found on lotus leaves (Nelumbo nucífera) is one of the models proposed which has been mentioned and typical model of biomimicry.[4] The self-cleaning properties of the lotus leaf surface are due to a micro-nano two-layer structure combined with hydrophilic wax crystals. According to Malshe's research group,[9,10] a novel non-wetting surface can be achieved with regular or random structures. Anti-wet surfaces have been applied to self-cleaning devices (high-rise building glass doors, windshields), anti-ice and snow protection (air conditioning cooling systems and refrigerators), and anti-fouling properties, science (marine ship hulls),[11,12] water collection (irrigation systems in arid areas).

Manufacturing techniques are also very diverse to accurately create structures using techniques such as lithography, laser printing, wet etching, or dry etching. By controlling prefixes such as concentration and reaction time, researchers are able to fabricate desired structures oriented to specific purposes.[3,13] The chemical coating techniques are also very diverse and depend on the properties that need to be equipped on the material, such as FluoroOrthorTetraSila ne and fluorocarbon compounds, which act similarly to the wax layer of lotus leave surface. However, fabricating a non-wetting surface requires techniques and high process control. Nanostructures are not easy to form on surfaces and will be easily destroyed if the parameters are not strictly controlled. Similarly, the hydrophobic chemical compound coating process also needs to be strictly established to ensure a perfect match between the nanostructure and the chemical layer thickness.[14,15] The current processes require expensive

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manufacturing techniques as well as complex and expensive manufacturing conditions.

In this study, we introduce the manufacturing of multi-functional surfaces on copper which is equipped with the ability to resist fouling, non-wetting, anti-adhesion, and water harvesting. The research will propose a quick, effective approach on common surfaces, oriented toward applications for devices with specific applications.

EXPERIMENTAL SETUP

Figure 1 describes the three-step functional surface fabrication process on Cu. First, the original Cu surface was cleaned with ethanol, acetone, and DI water. To generate nanostructures on the surface, the Cu samples have been pre-etched with hydrochloric acid for 10 min. After wet etching, the sample surface becomes wet with a contact angle of about 40°.

To achieve even higher roughness, the sample was enhanced etching with hydrofluoric acid to create a dense and sharp nanostructure [Figure 2a and b].[3] To fabricate a novel non-wetting surface, the etched sample was then covered with perfluoropolyether (PFPE) solvent for 1 h and then dried for another 1 h in the ambient air. After chemical coating, the surface demonstrated a very high water contact angle (>150°). The contact angle was calculated using a contact angle imaging device (Kyowa, Co., Ltd, Japan).

RESULTS AND DISCUSSION

Investigation of self-cleaning ability has been observed with a high-speed camera. Random-size-sand particles were spread randomly on the phobic cu functional surface tilted at a very small angle (from 1° to 2°). A volume of water (10 µL) was placed on the surface using a pipette and its movement was observed through a camera screen [Figure 2a and b]. Results recorded illustrated the complete removal of sand particles by water volume on its pathway, leaving a "clean" path (denoted by the yellow dashed line). In contrast, water on original copper and philic copper surfaces adheres to the surface due to hydrophilicity and therefore incapable of cleaning. This result also shows consistency with related studies on other material surfaces [Table 1].[2,16]

Low adhesion also was demonstrated in the perfectly elastic collision between water and the hydrophobic Cu surface [Figure 3]. Images from a high-speed camera showed the collision process of a water volume with initial kinetic energy (dropped from a height of 1 m) to initially verify the image of rain falling in reality. Upon further analysis, the process of water contacting the surface of hydrophobic Cu resembled a balloon as the water spread across the surface, quickly shrank, and bounced back into the air. The reason for this elasticity would be explained by the electrostatic attraction between the molecules at the surface of water and the hydrophobic Cu surface. After being functionalized, the surface prevented water from expanding the adhesion area on the surface. This contact pattern shows a consistent correlation with related research on silicon or iron surfaces and opens up research directions for anti-ice and dirt resistance because water cannot adhere to the surface.[17,18]

In addition, the results of investigating ice resistance with bond strength criteria are shown in Figure 4 with the correlation of water collection ability on surfaces with different wettability. A constant volume of water was gently placed on the surfaces

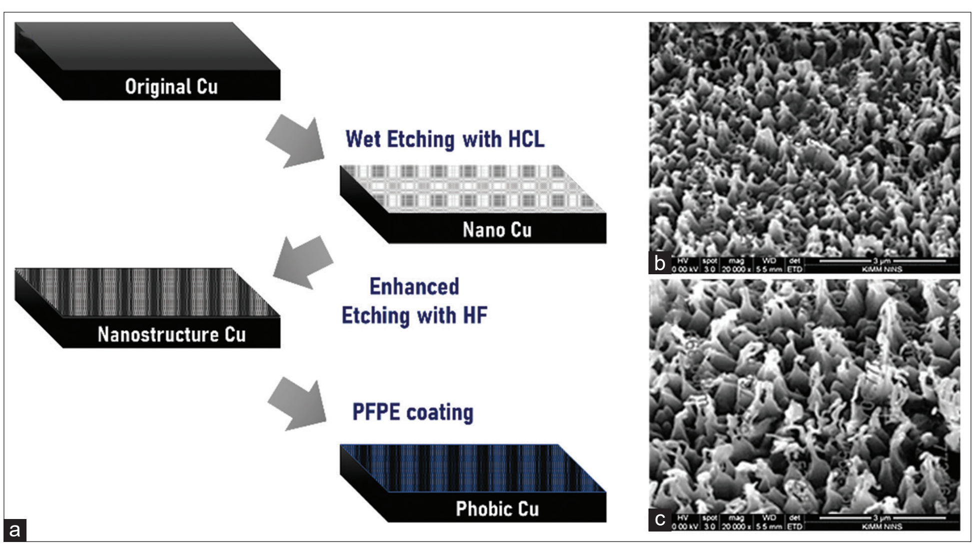

Figure 1: Functional surface fabrication process (a) and surface structure investigated by scanning electron microscopy with different magnifications (b and c)

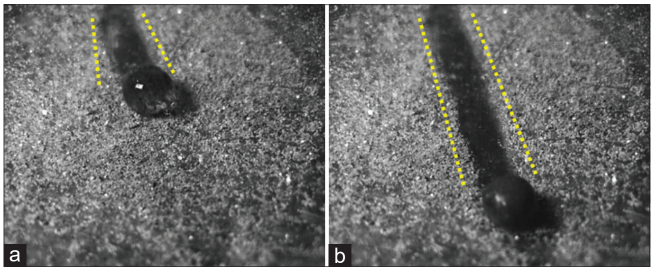

Figure 2: (a and b) Water self-cleaning on a hydrophobic Cu surface

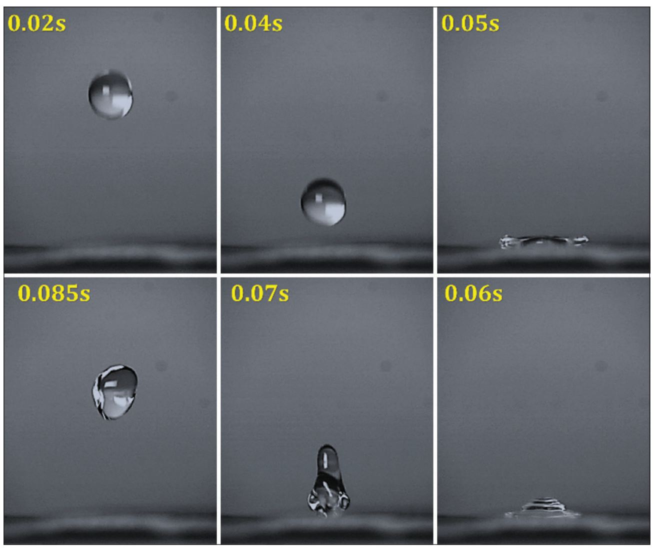

Figure 3: Images captured from high-speed video of the impact process of water drops on the surface of hydrophobic Cu

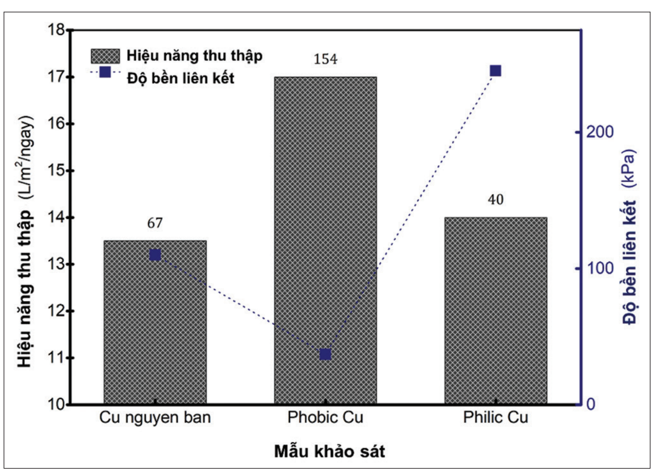

Figure 4: Results of surveying the ability to resist snow and ice and collect water of samples manufactured on Cu substrate

and cooled until solidification. A force sensor was controlled and moved horizontally to push the ice block until it was separated from the surface. The applied force recorded by the force sensor will be displayed on computer screen. The adhesion strength was determined as the maximum value recorded on the software. It can be seen that there was a linear relationship between bond strength. The higher adhesion we recorded, the lower contact angle we can observe, i.e., the more difficult for ice removal. This can be explained from the wettability point of view when the contact area will be larger if the hydrophilicity is higher, meaning the ice-surface contact area is larger, hence, ice breaking will be even more difficult.[15]

Table 1: Information and survey results on functionalized samples

STT	Sample	θ (°)	Adhesion strength (kPa)	Water collection (L/m^2/day)
#1	Original Cu	67	110	13.5
#2	Hydrophobic Cu	154	37	16.9
#3	Hydrophilic Cu	40	245	13.9

In contrast to the thin film water morphology on the original Cu (#1) and hydrophilic Cu (#3) samples, droplet condensation was observed on the phobic (#2) surfaces. This is achieved thanks to the chemical coating combined with nanostructures that create a Cassie-Baxter state at the interface, providing higher water collection performance compared to other surfaces.[19] The water collection survey results between the original Cu and hydrophilic Cu samples did not show much difference although the wet adhesion was quite different. The value recorded on the original surface is about 13.5 L/m^2/day whereas hydrophilic Cu can collect about 13.9 L/m^2/day. These two samples have completely different microstructures. While the original Cu has a flat surface, the hydrophilic Cu has undergone a corrosion process that integrates the structures [Figure 1]. We believe that thanks to the much higher contact area exposed to the moist gas flow compared to the original Cu sample, the hydrophilic Cu surface absorbed and promoted the phase transition process faster. However, due to greater wet stickiness, the ability to move water volumes would be more difficult. This would be a correlation between two parameters: The ability to promote phase transitions due to large areas and the mobility of water. This may be the reason that these two surfaces showed much difference. The larger the surface contact area, the less flexibility and vice versa!

The highest value belongs to the hydrophobic Cu sample when it might collect about 17 L/m^2/day, outperforming the other two samples. The hydrophobic Cu sample has a morphologically similar structure to philic Cu when both undergo wet corrosion, therefore the contact area was optimized to absorb water in the air to ensure phase transition. However, the hydrophobic Cu surface was also equipped with a layer of non-wet compound, thereby maximizing the mobility of water on the surface. The water will quickly move downward when it reaches the critical volume owing to high mobility. This volume would be determined by calculating the balance between its adhesion to the surface and gravity. With non-wet surfaces such as hydrophobic Cu, this volume will be very small due to the loose bond between the liquid and the surface. The water was quickly falling, leaving the surface dry, and continuing the phase change process. In other words, the hydrophobic Cu surface will not only have a large contact area to collect water but also ensure high mobility for water formed on it. This would be the reason hydrophobic Cu revealed superior collection ability compared to the remaining samples.

CONCLUSION

In this work, we present a method for fabricating anti-fouling and low adhesion, water collection surfaces based on the nature of the wet non-adhesion phenomenon. The copper surface was wet-etched to form regular fibrous nanostructures with a height of 200–300 nm. After functionalization with PFPE, the surface achieved a completely non-wet state and demonstrated good stain resistance. In particular, the fabricated surface also introduced good application in anti-icing and anti-adhesion when documenting the water-bouncing effect. The investigation on bond strength and water collection measurements also revealed advantages over other surfaces and proposed potential for a variety of application orientations.

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