

A one-step process to engineer superhydrophobic copper surfaces

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Abstract

Superhydrophobic surfaces are conventionally prepared employing two steps: roughening a surface and lowering their surface energy. In the present work, a direct voltage (DC) is applied between two copper plates immersed in a dilute ethanolic stearic acid solution. The surface of the anodic copper electrode transforms to superhydrophobic due to a reaction between copper and stearic acid solution. The fabrication process of superhydrophobic copper surfaces is simplified in just one-step. The surface of the anodic copper is found to be covered with flower-like low surface energy copper stearate films providing the water contact angle of $153 \pm 2^\circ$ with the roll-off properties.

Keywords : One-step process; Superhydrophobicity; Copper surface; Water contact angle; Scanning electron microscopy; X-ray diffraction

1. Introduction

Superhydrophobicity has recently become a very popular field because of its scientific and technological importance and wide range of applications in diverse areas. The most common areas where superhydrophobic surfaces attract attention are corrosion resistance, eyeglasses, self-cleaning windshields for automobiles, anti-sticking of snow or ice, windows, and many others [1], [2] and [3]. Various techniques have been devoted to prepare superhydrophobic surfaces, such as sol–gel [4], chemical etching [5], photolithography [6], electrochemical deposition [7], lithographic process [8], etc. The approaches used in making a surface superhydrophobic emphasize the importance of a combination of micro-nanoroughness on the surface and low surface energy as nature teaches us [9]. Previously, we have reported several superhydrophobic surfaces fabricated with water roll-off properties using various methods [1], [5], [10], [11], [12],

[13] and [14]. Mostly, the techniques used involve the conventional two-step procedure in which a surface is first roughened and then modified to lower the surface energy. Creation of certain micro-nanoroughness as a first step promotes the entrapment of air in the space between the rough features; and lowering the surface energy as a second subsequent step helps reduce the affinity of water drops with the low energy surface thereby weakening the water-surface interaction.

In the present study, the fabrication of superhydrophobic copper surfaces is reported using a one-step process by immersing copper electrode in the stearic acid solution with the application of DC voltage, simplifying the complexity of two different steps involved in the conventional methods. The transformation of hydrophilic copper surfaces into superhydrophobic surfaces in this process is due to the formation of low surface energy flower-like morphological feature of copper stearate.

2. Experiment

One-inch-square copper substrates were ultrasonically cleaned in a soap solution for 30 min for degreasing, followed by oxide removal by immersing in 10 vol. % HNO_3 and rinsing in water and ethanol. The cleaned substrates were immersed in an ethanolic stearic acid solution (0.01 M) and a DC voltage of 30 V was applied. The anodic and cathodic copper plates were separated by a distance of 1.5 cm. The surface of the anodic copper electrode turns blue due to the application of DC voltage. The morphological and elemental analyses of the anodic copper were performed using a scanning electron microscope (SEM, JEOL JSM-6480 LV) equipped with energy dispersive X-ray spectroscopy (EDX). The X-ray diffraction (XRD) analyses of the samples were carried out using a Bruker D8 Discover system. The wetting characteristics of the samples surfaces were carried out using a First Ten Angstrom contact angle goniometer.

3. Results and discussions

SEM studies of the copper surfaces reveal the evolution of different morphological features as a result of application of 30 V DC voltage at varying time, namely, 0.5 h, 1.5 h, and 3 h, as shown in Fig. 1(a–c). A reaction between the anodic copper and the ethanolic stearic acid electrolyte due to an applied DC voltage results in the formation of flower-like morphological pattern on the anodic copper surface as shown by a high magnification SEM image in Fig. 1(d). It can be seen that a closely packed uniform

coating (Fig. 1(a)) obtained on the surface prepared with 0.5 h of coating time. The formation of micro-size particles appears on the copper surface when the time of coating was increased to 1.5 h.

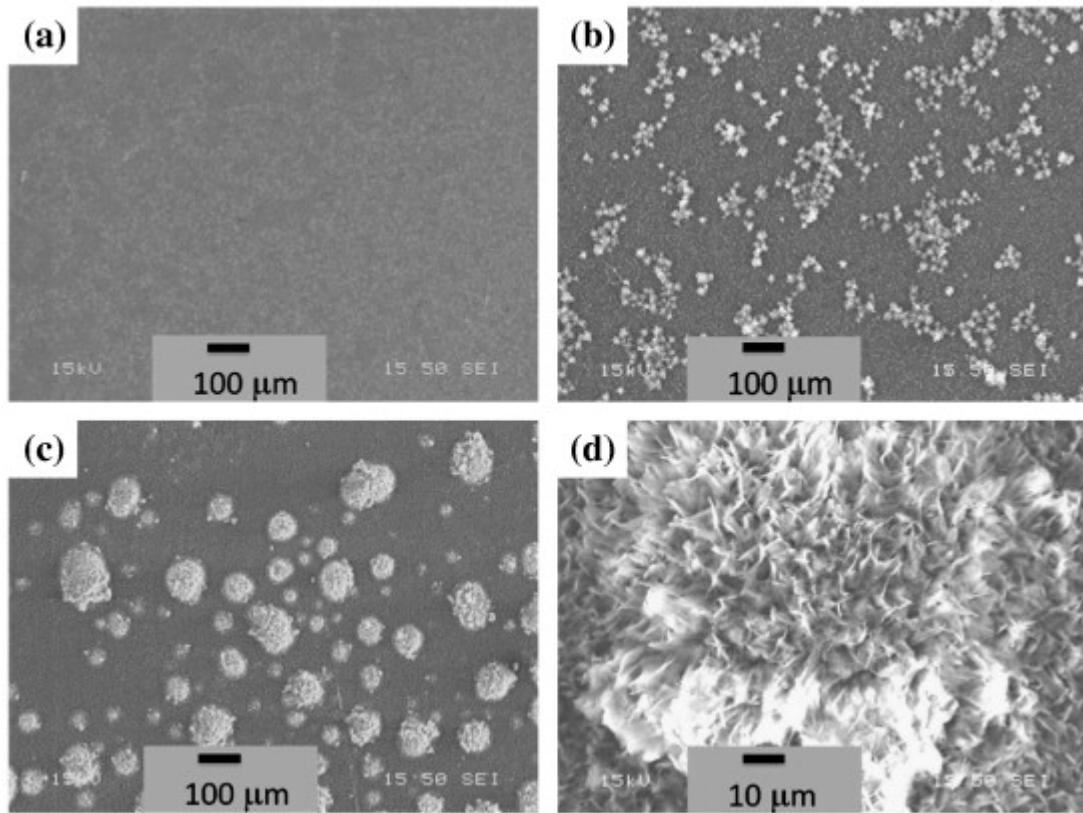


Fig. 1. SEM images of the anodic surface of the copper electrode after the application of 30 V DC voltage in an ethanolic stearic acid solution for (a) 0.5 h, (b) 1.5 h, (c) 3 h, (d) the morphology of a single particle as observed after 3 h.

It is however evident from Fig. 1(c) that prolongation of coating time to 3 h resulted in the formation of a rough surface with features revealing flower-like microstructures of ~ 50–100 μm. The SEM image of the individual flower-like microstructure (Fig. 1(d)) showed that each flower is composed of several tiny nanofibres clustered together to resemble a flower. It can be seen in Fig. 1(c) that these micro-nanoflowers are distributed randomly resulting in a micro-nanorough surface comparable to that of the lotus leaves promoting entrapment of air beneath a water drop placed on its surface [9].

Further analyses of the surfaces were carried out using X-ray diffraction (XRD). Fig. 2 shows the XRD patterns of the different surfaces as compared to a clean copper substrate recorded in the lower angle of 2θ range of 3–11°. The four distinct peaks

appearing in the spectra are assigned to copper stearate ($(\text{CH}_3(\text{CH}_2)_{16}\text{COO})_2\text{Cu}$) [15] resulting from a reaction between stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) and copper upon application of DC voltage. The intensity of copper stearate peaks are found to increase with the increase of deposition time due to the increase of thickness. This observation is complementary with the SEM analysis (Fig. 1(a–c)), where an increase in the time of applied voltage results in an increase in the dimensions of the flower-like micro-nanostructures. The appearance of the copper stearate peaks in the XRD patterns confirms the presence of low surface energy methylated (CH_3 and CH_2) components on the copper surfaces. Recently, we have demonstrated the formation of flower-like silver films on copper surface by electro-less deposition process where benzoic acid organic molecules were added in the silver nitrate solution to promote the superhydrophobicity of the silver coated copper substrates [14]. There, we reported the formation of copper benzoate which was responsible for the lowering of the surface energy and thereby resulting in superhydrophobicity of the flower-like silver films [14]. However, in the present study, we report the formation of single phase micro-nanoflowers morphology of copper stearate on copper substrates.

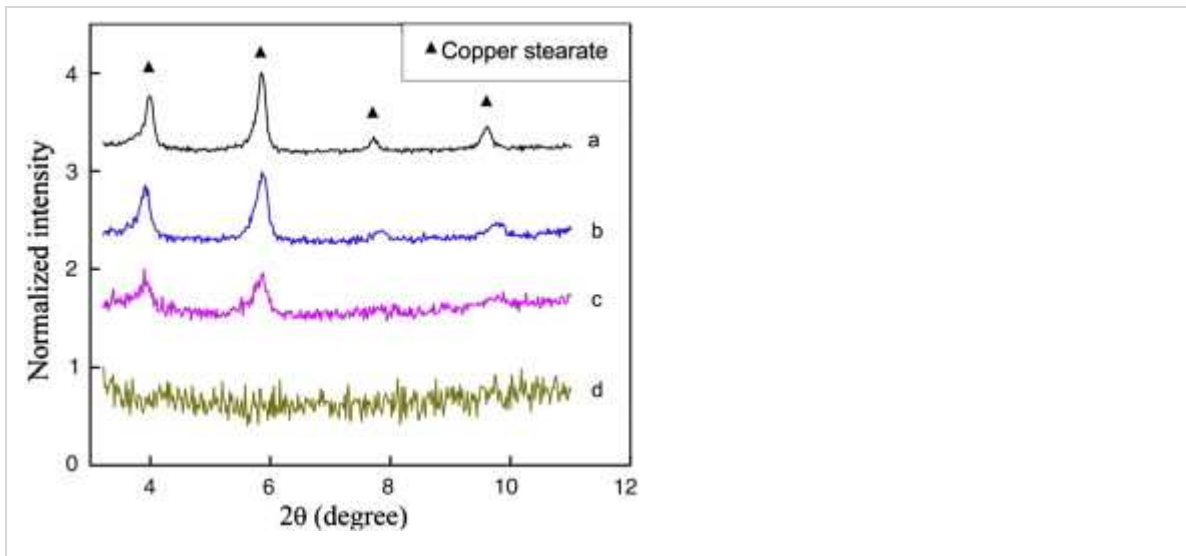


Fig. 2. XRD patterns of the anodic surface of the copper electrode after the application of 30 V DC voltage in an ethanolic stearic acid solution for (a) 0.5 h, (b) 1.5 h, (c) 3 h and (d) bare copper substrate.

Presence of flower-like micro-nanorough morphology and the low surface energy copper stearate together transform the copper surfaces to superhydrophobic. The wetting characteristics of these surfaces were characterized by measuring the water contact

angles and contact angle hysteresis. Fig. 3(a) shows the water contact angle variation as a function of time of the application of DC voltage demonstrating an increase in contact angle with the increase of time. A contact angle value of only $134 \pm 1.5^\circ$ obtained on the surface coated for 0.5 h increased to $153 \pm 2^\circ$ on the surface coated for 3 h which demonstrated water roll-off properties. The inset of Fig. 3(a) shows the shape of water drops for the two different time of deposition. The contact angle hysteresis, which is the difference between the advancing and receding angles recorded during the motion of a water drop, decreased from $\sim 32.6 \pm 2^\circ$ on the 0.5 h coated surface to as low as $\sim 1.3 \pm 0.5^\circ$ on the surface coated for 3 h (Fig. 3(b)).

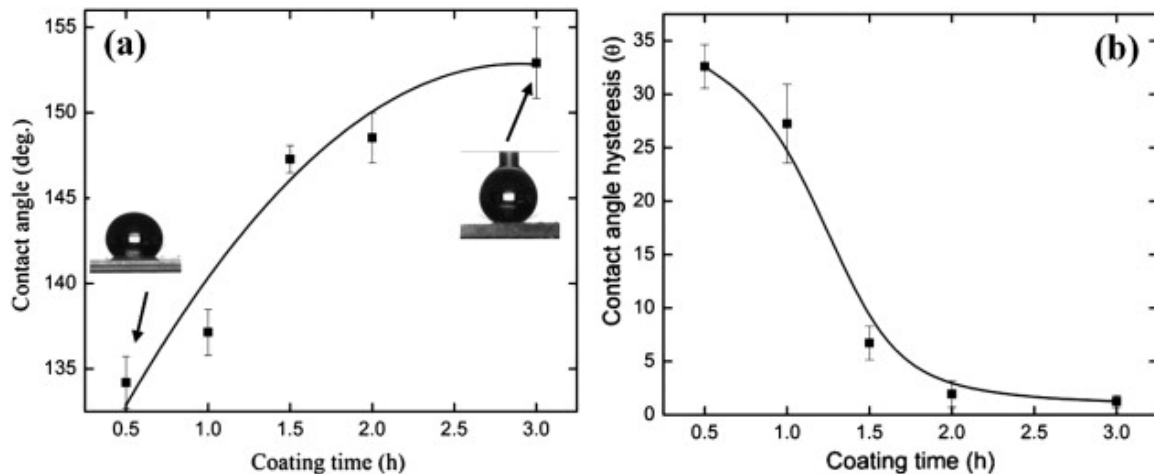


Fig. 3.

(a) Water contact angle and (b) contact angle hysteresis of anodic copper electrode with the application of 30 V DC voltage in an ethanolic stearic acid solution. The insets show the water drops on the copper surfaces coated for 0.5 h and 3 h.

The water drop remains stuck on the surface which provided very high contact angle hysteresis; however, the drop becomes unstable and starts to roll-off on the surfaces which provided very low contact angle hysteresis. The increase in water contact angle and the decrease in contact angle hysteresis at 3 h of time of application of DC voltage can be attributed to the co-existence of the micro-nanorough surface morphology with increased dimensions of the flower-like micro-nanofeatures (Fig. 1(c)) and the increased intensity of low surface energy copper stearate (Fig. 2), together reducing affinity of water toward the surface. Recently Sarkar et al., reported the formation of superhydrophobic copper surfaces with the deposition of silver films by galvanic exchange reaction both in one-step [14] and two-steps processes [10]. In the present

study, the one-step process employed to obtain superhydrophobic copper surfaces is much simpler than what we had reported earlier [14].

4. Conclusion

The one-step deposition process has been utilized to prepare superhydrophobic copper surfaces. In this process, the copper electrodes were immersed in the stearic acid solution and was applied a DC voltage. Morphological and structural analyses of the anodic electrodes show that the surface composed of micrometer size flower-like particles of copper stearate. The anodic copper electrode shows superhydrophobic properties with water contact angle of $153 \pm 2^\circ$ with the rolling off properties of water drops.

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