



Reversible wettability between superhydrophobicity and superhydrophilicity of Ag surface

Sheng Lei¹, Fajun Wang², Wen Li^{2*} and Guanjun Qiao³

ABSTRACT We present a facile one-step method to fabricate superhydrophobic Ag surface by electrodeposition without using any low surface energy reagent. The water contact angle of the prepared surface is 167.1° and the sliding angle is only 0.5° after heat treatment. It is demonstrated by the field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses that the dendrites of rough micro-nanostructure combined with the spontaneously adsorbed hydrocarbon make the surface exhibit superhydrophobicity. However, the superhydrophobic Ag surface becomes superhydrophilic when the surface is irradiated by UV light for several hours. It recovers superhydrophobicity after further heat treatment and can successfully implement the reversible wettability transition between superhydrophobicity and superhydrophilicity for several cycles.

Keywords: superhydrophobicity, superhydrophilicity, Ag surface

INTRODUCTION

It is well known that wettability is one of the most important properties of the solid material surface [1]. Superhydrophobicity is an extreme aspect of wettability with water contact angle (CA) more than 150° and sliding angle (SA) less than 10°. It has attracted utmost interest of many researchers [2–4] for various potential applications in the fields of self-cleaning [5–7], corrosion resistance [8,9], anti-icing [10–13] and oil-water separation [14–16]. Generally, the material surface modified with low surface energy reagent and constructed micro-nanostructures are two common ways to fabricate the superhydrophobic surface [17–21]. Up to date, a lot of artificial superhydrophobic surfaces have been successfully prepared by various methods. However, most methods are complicated

and still in need of the chemistry of surface modification which is seriously harmful to the environment and hinders its large-scale application in engineering [22,23]. Therefore, a simple and fast method to prepare the superhydrophobic surface has an obvious prospect in the industrial application. In addition, superhydrophilicity, the other extreme wettability state of surface, that water contact angle less than 10°, also has attracted most attentions from theoretical investigation as well as industrial applications [24–26]. Inspired by the creatures of superhydrophobicity or superhydrophilicity in nature, smart functional materials with switchable extreme wetting behaviors must have greater value and application prospect [27,28], such as tunable wettability devices, rapid water motion, quick wetting responsiveness, smart separation membranes and controlled transportation of fluids.

In this article, we developed a facile and fast method to fabricate superhydrophobic Ag surface on brass substrate by electrodeposition in AgNO₃ solution. The surface exhibited excellent superhydrophobicity without using low surface energy reagent and only after heated at 200°C for 10 min. What's more, the superhydrophobic Ag surface turned into superhydrophilic by UV light irradiation for several hours. Most interestingly, the superhydrophobic Ag surface can be achieved again after heat treatment. The Ag surface with reversible wettability was obtained successfully.

EXPERIMENTAL

Materials and reagents

Brass foils were obtained from Chong Rui Metal Material Co., Ltd., China. Silver nitrate (AgNO₃) and ethanol were

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purchased from Shanghai Chemical Reagent of Chinese Medical Group. SiC sandpapers with a grade of 1200# were supplied by 3M Company.

Sample preparation

Brass foil of 40 mm×20 mm was polished by 1200# sandpaper and then cleaned with deionized water and ethanol as the working electrode. Electrodeposition was performed in 0.001 mol L⁻¹ AgNO₃ solution by an LW10J5 two-electrode system electrochemical workstation with the graphite sheet as the counter electrode. The electrodeposition worked in a potentiostatic mode of 3.5 V at 25°C. Then the samples were washed several times with deionized water and ethanol, respectively. The superhydrophobic Ag surface was obtained after heat treatment in an oven at 200°C for 10 min.

Characterizations

The sample surface morphologies were determined by a field emission scanning electron microscope (FESEM, FEI-Nova NanoSEM-450, America). The crystal structure of the samples was measured by X-ray diffraction (XRD, Bruker SMART APEX II, Germany). The chemical

compositions of the samples were studied by X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., UK). The water CAs and SAs were studied with 6 μL water by an optical contact angle meter (DSA 20, Krüss, Germany). UV irradiation was performed with a 40 W UV lamp (UVA-340, China).

RESULTS AND DISCUSSION

The surface morphologies of the brass surface after different electrodeposition time were investigated by FESEM as shown in Fig. 1. There are only scratches on the bare brass surface before electrodeposition (Fig. 1b). For the brass deposition time of 30 s, the surface is covered with uniform nanoparticles sized in 10 to 30 nm and the surface got rough clearly (Fig. 1d). When the deposition time increased more than 60 s, the density and size of nanoparticles increase to form clusters (Fig. 1f) and begin to grow out typical dendrites with branched fractal structure, which make the surface become rougher (Fig. 1h). The longer the deposition time is, the higher density of clusters and dendrites are on the brass surface whose coverage area is also increased (Fig. 1j). The surface is completely coated by dendrites micro-nanostructures layer upon layer (Fig. 1l)

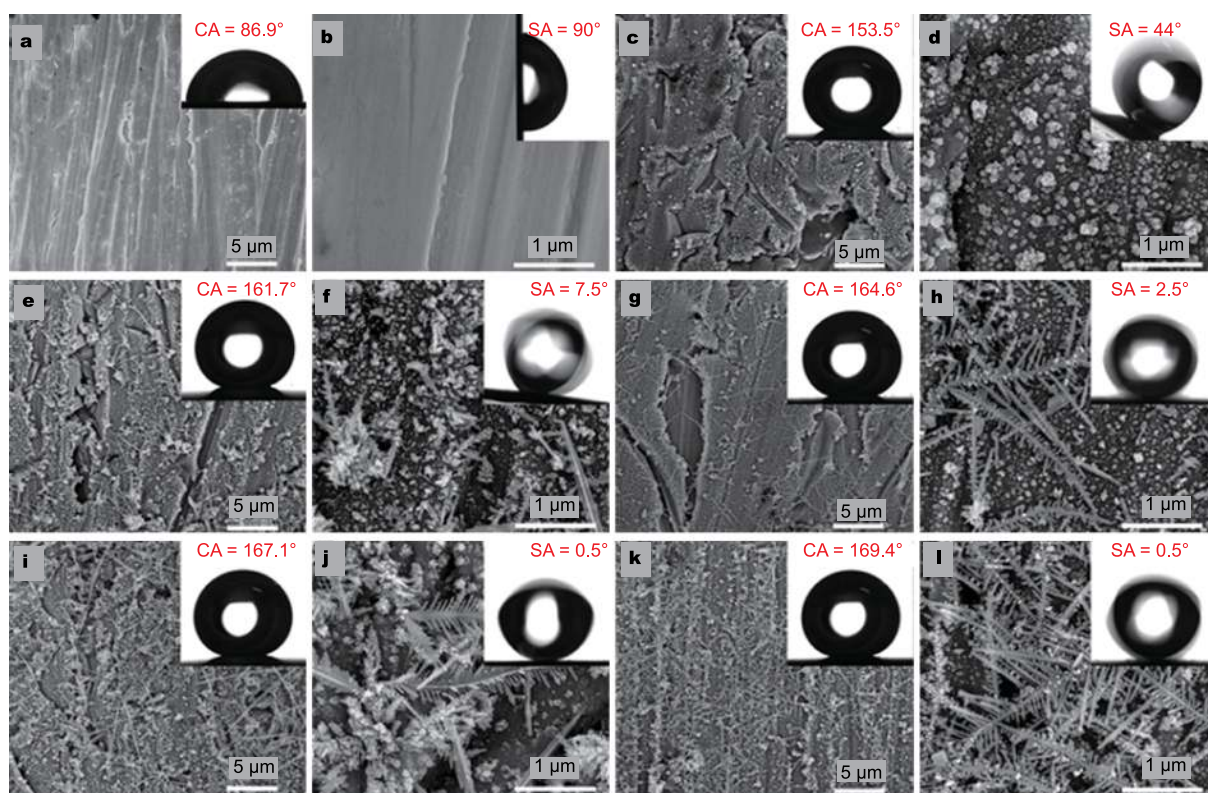


Figure 1 FESEM images of the brass surfaces after different electrodeposition time: (a, b) 0 s; (c, d) 30 s; (e, f) 60 s; (g, h) 120 s; (i, j) 180 s and (k, l) 300 s. The insets show the optical images of water CA and SA.

when the deposition time is prolonged to 300 s, and the surface is very rough. The electrodeposition time plays an important role in determining the surface structure and the surface roughness. The layers of dendrites micro-nanostructures on the brass surface formed lots of voids, which are favorable to trapping a large amount of air, and thus effectively increase the water-air interface and prevent the penetration of water droplets into the surface.

In this work, heating is a key step for the electrodeposition surface changing from superhydrophilic to superhydrophobic. Without heat treatment, the electrodeposition surface is superhydrophilic with water contact angle less than 10° . However, the surfaces of different electrodeposition time show the superhydrophobicity after heat treatment at 200°C for 10 min. It can be clearly seen that the CA increases and SA reduces with increasing electrodeposition time in Fig. 1 insets.

As we all know, surface roughness plays a crucial role in the contact angle and the wetting ability. Figs 2c and d show the FESEM images of the surface of the electrodeposition time for 300 s with heating treatment at 200°C for 1 h. Comparing with the electrodeposition surface before heating (Figs 2a and b), the roughness and the dendrites micro-nanostructures of the surface after heating treatment have no obvious change. It is believed that the roughness of the prepared superhydrophobic surface is not destroyed by heating treatment for just 1 h.

The wettability of solid material surfaces depends on both the surface chemistry and surface roughness. The crystal structure of the prepared superhydrophobic Ag sur-

face in Fig. 11 was analyzed by XRD and the results are shown in Fig. 3. In contrast to the brass surface, three new peaks at 2θ of 38.3° , 44.2° and 64.5° of the superhydrophobic Ag surface correspond to (111), (200) and (220) planes of the crystalline Ag (JCPDS No. 04-0783) [29,30], respectively. It indicates that there is no impurity phase of Ag_2O [30] or Cu_2O [14] generated after heat treatment, which has hydrophobicity.

To further confirm the superhydrophobic Ag surface composition and chemical state, a more sensitive technique XPS was adopted. As observed in Fig. 4a, there were five elements in the survey scan spectrum, C, O, Ag, Cu and Zn. Cu and Zn belong to the brass substrate [see Supplementary information Fig. S1]. The peaks of Ag 3d in Fig. 4b centered at 368.3 and 374.3 eV correspond to the binding energy of Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively, which agrees well with metallic Ag [30]. The high-resolution spectrum of C 1s is shown in Fig. 4c, and two peaks located at the binding energies of 284.7 and 288.6 eV are attributed to C–C/C=C/C–H and C=O/COOH, respectively. The peak of C–C/C=C/C–H plays a predominant role which reduces the surface energy [31–33]. The O 1s spectrum shown in Fig. 4d has a peak at 531.6 eV which can be attributed to the C=O–OH [33]. Therefore, the XPS measurements confirm the existence of Ag and spontaneously adsorbed carbon contaminant on the superhydrophobic Ag surface.

Further more, the prepared surfaces were heated at different temperatures from 50 to 100, 150, 200 and 250°C with the time to exhibit superhydrophobic shortened from 6.5, 1 h, 25, 10 to 3 min. However, it needs several weeks to achieve superhydrophobicity without heating at ambient

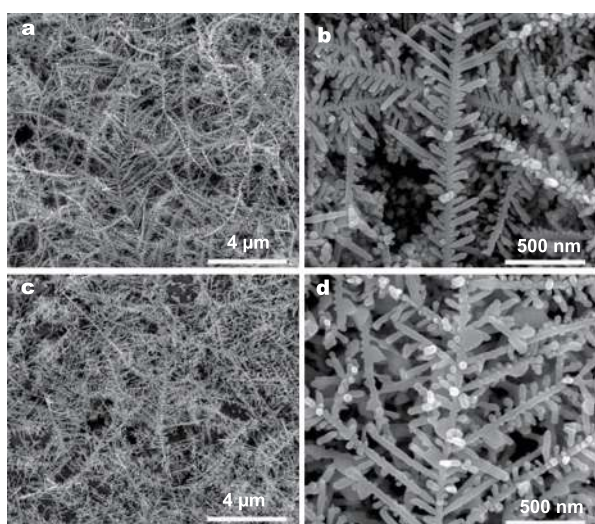


Figure 2 FESEM images of the electrodeposition surface before (a, b) and after (c, d) heat treatment.

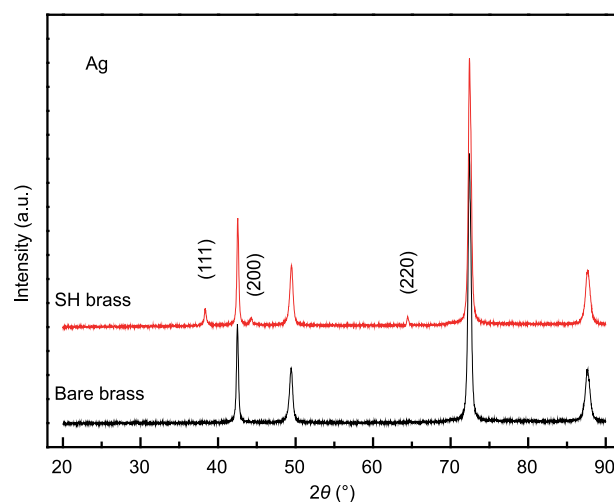


Figure 3 The XRD patterns of the prepared superhydrophobic Ag surface in Fig. 11.

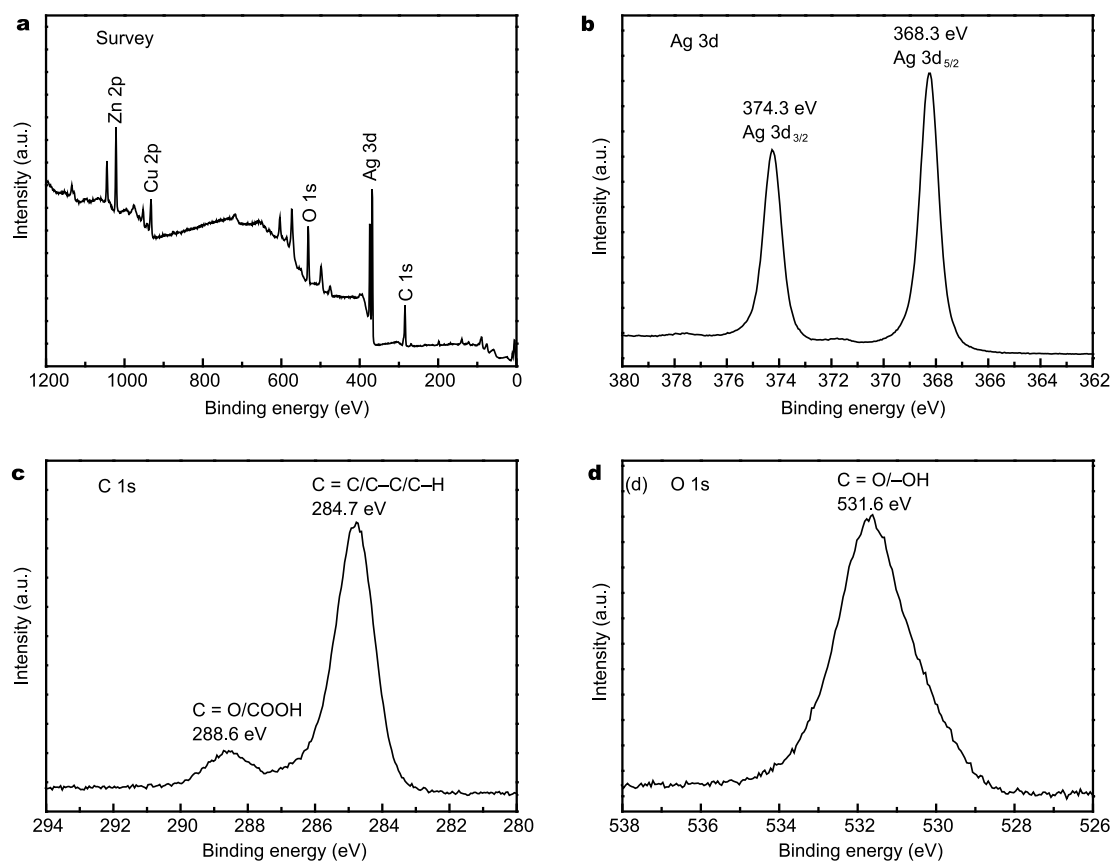


Figure 4 The XPS spectra: survey (a), Ag 3d (b), C 1s (c) and O 1s (d) of the prepared superhydrophobic Ag surface in Fig. 11.

temperature. The experimental results indicate that the speed of the Ag surface to reach superhydrophobic becomes faster as the temperature rise. The heating treatment does not damage the surface dendrites structure but change the wetting property. This is because of the hydrocarbons containing non-polar groups of C=C/C-C and polar groups of C=O/C-O existing almost everywhere in air that can spontaneously adsorb on the material surface [34,35]. Both of the non-polar and polar hydrocarbons are gradually desorbed during the heating process. While the desorption speed of the polar group is higher than that of the non-polar group, which reduces the surface energy to a critical value that below the water. As a result, the surface energy of Ag surface decreases and the contact angle increases with the increasing of both temperature and time. The superhydrophobic Ag surface was also obtained even when heated in the vacuum chamber.

To get more information of the adsorbed hydrocarbons, more XPS analyses of the Ag surface before and after heat treatment were presented in Fig. 5. After heat treatment, the relative intensities of the C 1s increases obviously with the atom percentage from 47.01 to 52.14, the atomic per-

centage of O 1s slightly increases from 20.62 to 21.07. It is confirmed that the non-polar groups of C=C/C-C are the main adsorbed carbons, while the polar groups of C=O/COOH in the adsorption quantity are very few. Additionally, a pure silver plate with 3 mol L⁻¹ HNO₃ is etching for 30 min, and the water CA of the surface increases from 18.7° to 116.5° after being heated at 200°C for 10 min. These results indicate that the adsorbed hydrocarbon and dendrites rough micro-nanostructure of the Ag surface work together to achieve the superhydrophobicity.

To investigate the effect of UV irradiation on the wettability of the superhydrophobic Ag surface, the change of water CA of the surface with UV irradiation time is presented in Fig. 6 in detail. The insets show the optical images of water CA. It can be seen that the water CA reduces rapidly from 167.1° to 7.8° when the UV irradiation time increases. The process of superhydrophobic Ag surface becoming superhydrophilic only needs 6 h of UV irradiation [35,36]. These phenomena can be explained by two aspects. Firstly, most adsorbed hydrocarbon of superhydrophobic Ag surface is removed after UV irradiation treatment which increases the surface energy. Secondly,

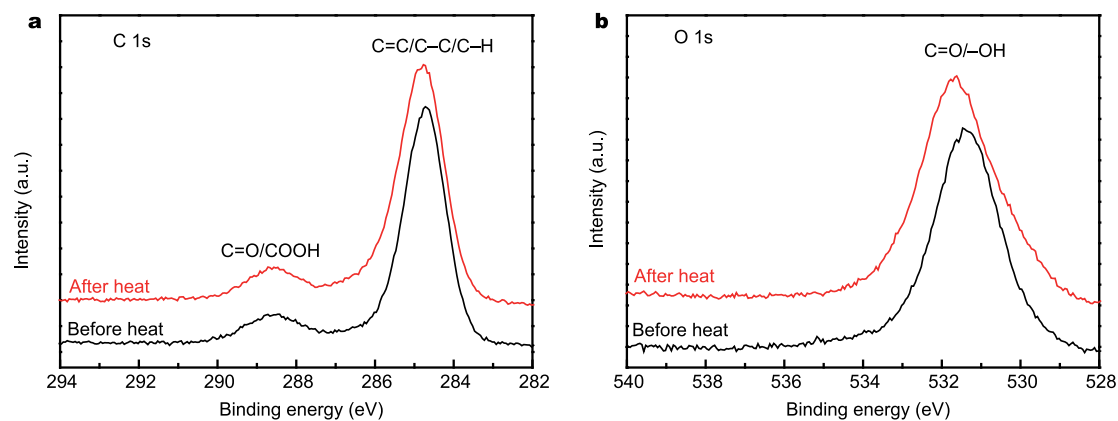


Figure 5 The XPS spectra of the Ag surface before and after heat treatment.

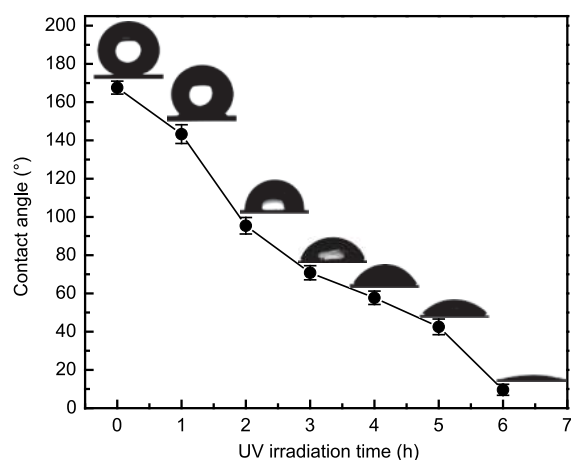


Figure 6 Variation of water CA with UV irradiation time.

part of the adsorbed hydrophobic groups are oxidized to hydrophilic groups due to UV irradiation. It is detected that the atomic percentage of the adsorbed carbon is 52.14 and oxygen is 21.07 on the Ag surface before UV irradiation. But the atomic percentage of the adsorbed carbon reduces to 44.56 while oxygen increases to 25.48 after UV irradiation [see Supplementary information Fig. S2]. This results in the higher surface energy inducing the transformation of superhydrophobic to superhydrophilic.

However, the superhydrophilic Ag surface with UV irradiation is recovered rapidly to the original superhydrophobic state by heating at 200°C for only 10 min. The reversible wettability transition could be repeated more than five cycles, and a good reproducibility between superhydrophobicity and superhydrophilicity in terms of the water CA is observed in Fig. 7. Additionally, the superhydrophilicity of Ag surface also could recover to superhydrophobicity at room temperature, but it needs more than four weeks.

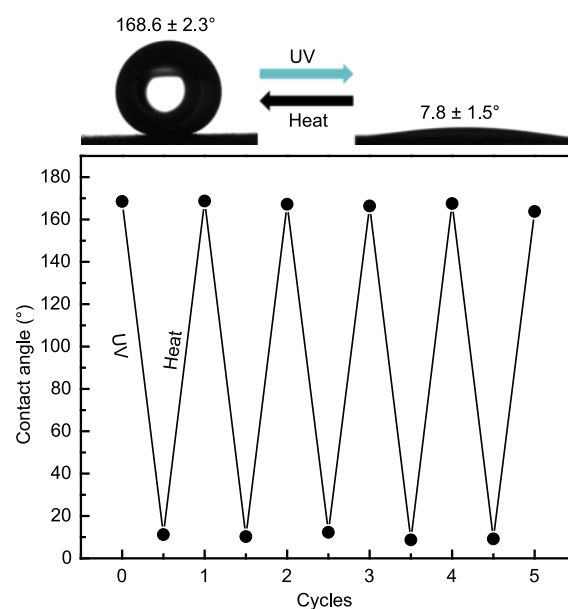


Figure 7 Reversible wettability transition of the Ag surfaces by UV irradiation and heat treatment.

CONCLUSION

In conclusion, a superhydrophobic Ag surface of reversible wettability transition was fabricated on brass by a facile method of electrodeposition. The heat treatment accelerated the surface adsorption of airborne hydrocarbons in air which could reduce the surface energy. The dendrites rough micro-nanostructure and the spontaneously adsorbed hydrocarbon function together for the surface superhydrophobicity. The reversible wettability between superhydrophobicity and superhydrophilicity of Ag surface was achieved with heat treatment and UV irradiation. In addition, the superhydrophobic Ag surface could also be prepared on stainless steel and part of conductive metal

substrates in the same way. It is believed that the rapid wettability transition of material surface is helpful to design smart devices and may have important potential applications.

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Supplementary information Supporting data are available in the online version of the paper.



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银表面超疏水性与超亲水性的可逆转变研究

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摘要 本文采用简单的电沉积法制备出无需低表面能试剂修饰的超疏水银表面. 镀银表面经过热处理后与水滴的接触角达到 167.1° 而滚动角仅为 0.5° . 通过FESEM, XRD以及XPS分析表明, 制备的微米/纳米级粗糙结构的银表面吸附了空气中的碳氢化合物导致表面具有超疏水性. 当用紫外光照射表面几个小时后, 表面会从超疏水性转变为超亲水性. 然而, 热处理后表面又恢复超疏水性能. 重复紫外光照射和热处理过程, 镀银表面可以实现超疏水和超亲水之间的多次转换.