Preparation of Ag superhydrophobic surface on metal substrates

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Abstract. In this work, the facile approaches are developed for preparation the Ag superhydrophobic surfaces (SHSs) on zinc (Zn), copper (Cu) and aluminium (Al) substrates. The water contact angles (WCAs) of the Ag SHSs on Zn, Cu and Al substrates are 167°, 165° and 154°, respectively. Furthermore, the water sliding angle (WSA) of each surface is less than 1°. The morphology and chemical composition of the samples are characterized using scanning electron microscopy (SEM) and X-ray diffraction pattern (XRD). The as-prepared three kinds of SHSs possess the self-cleaning performance, which can quickly take the chalk away when the water droplets fall down the SHSs. In addition, the superhydrophobicity of the SHSs can well maintain after exposure to the air for 6 months, indicating that the surfaces can sustain good stability.

1. Introduction

With the advent of new technologies, superhydrophobic surfaces (SHSs) have been constructed as interfacial materials, which exhibit high static water contact angles (WCAs) and ultra-low water sliding angle (WSA) [1]. Especially, SHSs have attracted tremendous attention due to their variety of special applications in the fields of self-cleaning, anti-icing, anti-corrosion, anti-biofouling, drug delivery and water–oil separation, *etc* [2-5]. There are numerous ways to construct superhydrophobic materials such as anodization [6], electrodeposition [7], sol-gel method [8], layer-by-layer deposition [9] and immersion process [10]. Generally speaking, on account of its facileness, low cost and suitability for industrial applications, immersion process is considered as an effective technique to prepare the SHS. Thus far, substrates, such as glass, polymers, metals, waxes, and semiconductors, have been investigated for SHSs [11, 12]. The fabrication of SHSs on various metal substrates has attracted increasing attentions due to the manageable morphology and technological applicability of the metallic SHSs [13]. Furthermore, as a widely used engineering material, silver (Ag) is attractive because of its high electrical and thermal conductivity, malleability and mechanical workability, stability and bactericidal property. Therefore, it is meaningful to construct Ag SHSs on metal substrates for practical application of metals [14].

In this article, we successfully fabricated the Ag SHSs on zinc (Zn), copper (Cu) and aluminum (Al) substrates via etching, followed on replacement deposition and then annealing. The WCA of each substrate could reach to 150° and the WSA of each sample was less than 1°. Moreover, the prepared SHSs exhibited self-cleaning property and long-term stability.

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2. Materials and methods

2.1. Reagents and Materials

Silver nitrate ($AgNO_3$, 99.8%), sodium hydroxide (NaOH, 99.5%), nitric acid (HNO_3, 65~68 wt%), ammonia ($NH_3•H_2O$, 25~28%), acetone (C_3H_6O, 99.5%), ethanol (C_2H_5OH, 99.7%), sodium chloride (NaCl, 99.5%) were purchased from Beijing Fine Chemical Co. Ltd. China without further purification. Zn, Cu and Al sheets (99.9%, 1.0 cm×1.0 cm×0.1 cm) were obtained from Beijing Nonferrous Metal Research Institute.

2.2. Experimental sections

2.2.1. Fabrication of the Ag SHS on Zn substrate. Firstly, the Zn sheet was ultrasonically cleansed by immersion in ethanol and acetone for about 5 min, respectively, to remove the pollutants of the substrate. Then, the cleaned sheet was ultrasonically rinsed with deionized water and dried at ambient temperature. After that, the dried Zn sheet was immersed in 0.01 $mol•L^{-1}$ $AgNO_3$ aqueous solution for 30 min, and finally, annealed at 200 ºC for 1 h.

2.2.2. Fabrication of the Ag SHS on Cu substrate. In the first place, the Cu sheet was ultrasonically cleansed by immersion in ethanol and acetone for about 5 min, respectively, to remove the pollutants of the substrate. Then, in order to get rid of the oxide film, the cleaned sheet was ultrasonically cleansed in 26.7 wt% HNO_3 aqueous solution and rinsed with deionized water and ethanol. After dried at ambient temperature, the Cu sheet was immersed in 0.01 $mol•L^{-1}$ $AgNO_3$ aqueous solution for 30 min, and finally, annealed at 180 ºC for 12 min.

2.2.3. Fabrication of the Ag SHS on Al substrate. Firstly, the Al sheet was ultrasonically cleansed by immersion in ethanol and acetone for about 5 min, respectively, to remove the pollutants of the substrate. Then, the cleaned sheet was etched with 3 $mol•L^{-1}$ NaOH aqueous solution for 1 min to remove the oxide film and then ultrasonically rinsed with deionized water for 2 min. After that, the dried Al sheet was immersed in the mixture of 100 mL 0.01 $mol•L^{-1}$ $AgNO_3$ aqueous solution containing 3.6 mL $NH_3•H_2O$ for 9 min. And $NH_3•H_2O$ is used as a ligand combined with Ag^+ to change the potential of Ag^+ reduction as well as control the pH of the solution. Finally, annealed at 160 ºC for 20 min.

2.3. Characterization

The WCAs and WSAs of the samples were measured with a remote computer-controlled goniometer system (FTÅ 200, Data physics Inc, USA). All WCAs of the samples were measured five times on different positions with 8 μL water droplets at ambient temperature. The measuring error of the WCA value was ± 1°. The surface morphologies of the samples were characterized by a scanning electron microscope (SEM, S-4800, Hitachi, Japan). The surface composition of the samples was measured by X-ray powder diffractometer (XRD, D8 Advance, Bruker, Germany) with Cu Kα radiation (40 Kv, 40 Ma, and $\lambda = 0.15418$ nm) at a scanning rate of 3° min^{-1}.

2.4. Self-cleaning performance test

The self-cleaning property of samples was studied by observing the phenomena of the water droplets falling down the sample surfaces covered with chalk.

3. Results and discussion

3.1. Surface morphology and wettability

The surface morphologies of the sample surfaces were investigated by SEM as shown in figure 1, and the insets are the WCAs of the relative samples. Figure 1a, b and c reflect the sample morphologies of the bare Zn, Cu and Al with the relatively smooth surfaces, even though some scratches exist and the

WCAs of them are 54°, 76° and 65°, respectively. Figure 1a', b' and c' display the SEM images of the Ag SHSs on Zn, Cu and Al substrates, respectively. It can be seen that there are numerous micro/nano-structures caused by the acid/alkaline cleaning, deposition of Ag from the replacement reaction and the annealing process. The WCAs of the corresponding Ag SHSs are 167°, 165° and 154°, respectively. Similarly, in ref [13], they measured the value of WCA of the Ag SHS is 164°. But, in ref [15], the Ag coating is superhydrophilic. The similarity or different are due to the roughness and surface composition are appropriate or not. In summary, the rough surfaces, coupled with the appropriate annealing process play the crucial roles in effecting wettability of the SHSs. Furthermore, in the true sense, a SHS should not only have a large static contact angle, but also a small sliding angle. Undoubtedly, the as-prepared each Ag SHS with the WSA less than 1° exhibits non-sticking behavior, which allows droplets to slide easily when the water droplets are placed on the surface.

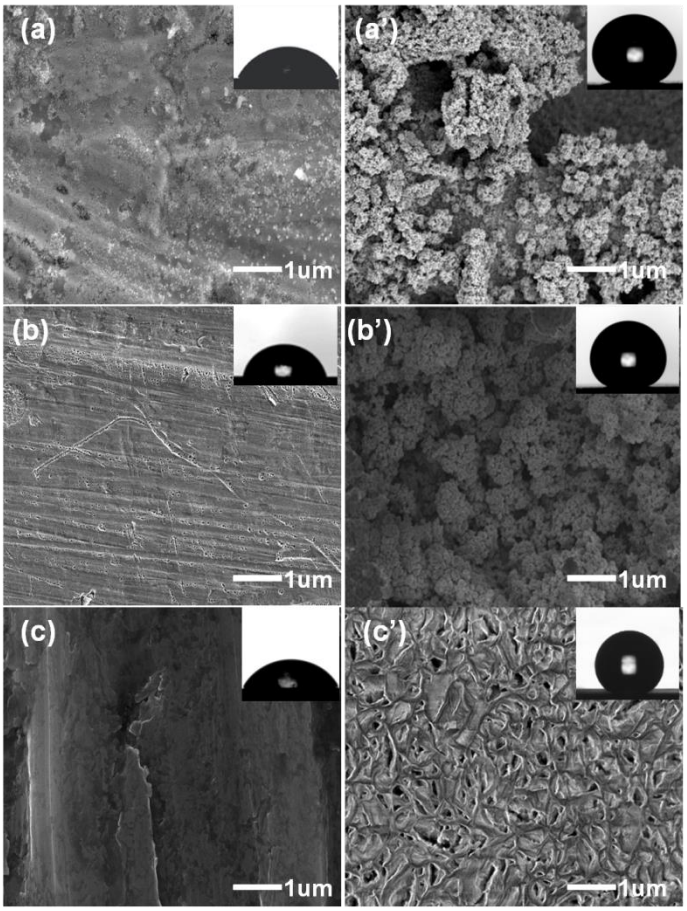


Figure 1. SEM morphologies of different samples: (a) pure Zn sheet; (a') Ag SHS on Zn substrate; (b) pure Cu sheet; (b') Ag SHS on Cu substrate; (c) pure Al sheet; (c') Ag SHS on Al substrate. The insets are the WCAs of relative samples, respectively.

Two models can account theoretically for the wetting properties. One is the Wenzel model [16], in which water drops will penetrate the grooves of the rough surface. However, Cassie *et al.,* through the studies of superhydrophobic phenomena in nature, found that when the water droplets are in contact with the solid surface, the water droplets cannot fully penetrate the grooves of the rough structure. Thus, the Cassie–Baxter model, where the SHS is regarded as a porous medium composed of air pockets, is always used as the calculation model [17]. The Cassie–Baxter state can be defined as follows:

$$\cos\theta^* = f_1 \cos\theta - f_2 \quad (1)$$

θ^* (the WCA of the SHS) is the apparent contact angle and θ (the WCA of pure metal substrate) is the intrinsic contact angle of the composite surface. f_1 is the fractional interfacial area of solid/water on the surface, f_2 is the fractional area of air/water and $f_1 + f_2 = 1$. The WCAs of the Ag SHSs on Zn, Cu and Al are all over 150° and the value of WCA of pure Ag surfaces is 79° [18]. According to Eq. (1), it can be obtained that the average value of f_1 is 0.112. This means that only less 11.2% of the area of water droplet directly contacts with the surface of the sample and the remaining more than 88.8% is in contact with air. Thus, the water droplets cannot penetrate the grooves, indicating the prepared SHSs are sufficiently rough and covered with the Ag micro/nano-structured.

3.2. XRD analysis

It is well-known that the wetting behavior of solid surfaces is governed by both the surface morphology and the chemical composition. The surface substance and crystal structure of samples are assessed by XRD spectra, as shown in figure 2.

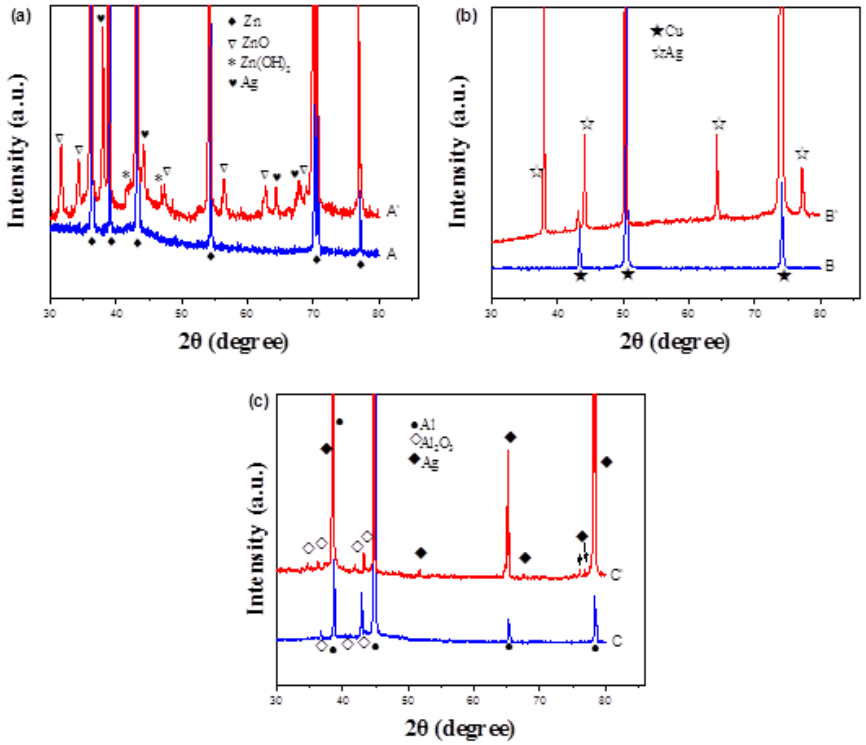


Figure 2. XRD spectra (a): pure Zn (A) and Ag SHS on Zn substrate (A'); XRD spectra (b): pure Cu (B) and Ag SHS on Cu substrate (B'); XRD spectra (c): pure Al (C) and Ag SHS on Al substrate (C').

The region of the 2θ is 30~80° and the scanning speed is 3°•min-1. The XRD spectra of pure Zn (A) and Ag SHS on Zn substrate (A') are shown in figure 2a. The symbols of • , , * and ♥ represent the characteristic peaks of Zn, ZnO, Zn(OH)2 and Ag, respectively. From curve (A), the sharp peaks mainly are attributed to the diffraction peaks of Zn. As shown in curve (A'), the peaks of ZnO and Zn(OH)2 appear, which indicates that some of Zn was oxidized in the reaction process. In addition, the sharp peaks showed at 2θ = 37.9°, 44.2°, 64.5° and 67.5° are attributed to the diffraction peaks of Ag(111), Ag(200), Ag(110), and Ag(106) (JCPDS card no.87-0598), which indicates that the Ag was successfully deposited on Zn substrate. In addition, the XRD spectra of pure Cu (B) and Ag SHS on Cu substrate (B') are shown in figure 2b, the symbols of ★ and ☆ represent the characteristic peaks of Cu and Ag, respectively. The three diffraction peaks at 2θ = 43.31°, 50.41° and 74.11° can be indexed to the Cu (JCPDS Card No. 04-0836) corresponding to Cu(111), Cu(200) and Cu(220),

respectively from curve (B). And after the fabrication process as shown in curve (B'), the diffraction peaks of Ag show up, which indicates that the Ag was successfully deposited on Cu substrate. In the same way, the XRD spectra of pure Al (C) and Ag SHS on Al substrate (C') are shown in figure 2c. The symbols of ●, ◇ and ◆ represent the characteristic peaks of Al, Al2O3 and Ag, respectively. There are only some peaks of Al and Al2O3 on pure Al surface as shown in curve C. But after the reaction as shown in curve C', the peaks at 2θ = 37.04°, 51.67°, 64.52°, 67.5°, 76.01°, 76.79° and 78.89° are attributed to the diffraction peaks of Ag(101), Ag(104), Ag(110), Ag(106), Ag(200), Ag(201) and Ag(202) (JCPDS card no. 87-0598). In summary, the results indicate that the hierarchical micro/nano coatings are successfully prepared on the three substrates.

Through the analysis of XRD of the SHSs, the chemical reaction equations for fabricating the three SHSs can be obtained and showed in scheme 1-3, respectively.

$$2Zn + O_2 = 2ZnO \quad (1)$$
$$ZnO + H_2O = Zn(OH)_2 \quad (2)$$
$$Zn + 2AgNO_3 = 2Ag + Zn(NO_3)_2 \quad (3)$$

Scheme 1 The reactions for fabricating Ag SHS on Zn substrate.

$$2Cu + O_2 = 2CuO \quad (4)$$
$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O \quad (5)$$
$$Cu + 2AgNO_3 = 2Ag + Cu(NO_3)_2 \quad (6)$$

Scheme 2 The reactions for fabricating Ag SHS on Cu substrate.

$$4Al + 3O_2 = 2Al_2O_3 \quad (7)$$
$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O \quad (8)$$
$$3AgNO_3 + Al = 3Ag + Al(NO_3)_3 \quad (9)$$

Scheme 3 The reactions for fabricating Ag SHS on Al substrate.

3.3. Self-cleaning property

The self-cleaning effect of SHS is a significant property due to the big WCA and the small WSA. In this experiment, the pure metal surfaces compared with the SHSs to study the self-cleaning property. As shown in figure 3, the text result of pure Al (A) and Ag SHS on Al substrate (B) are dusted with chalk powder. When the water droplets fall down the pure Al surface, the drops stick with chalk, and the dust still covers the Al surface finally. The same process is conducted for the Ag SHS on Al substrate, and the chalk can be promptly taken off the sample surface with rolling water droplets. In the same way, the tests results are consistent across the Ag SHS on Zn substrate and the Ag SHS on Cu substrate. These phenomena show that the SHSs are sufficiently rough because of the micro/nano structures, and this unique property makes the superhydrophobic materials have more widely application.

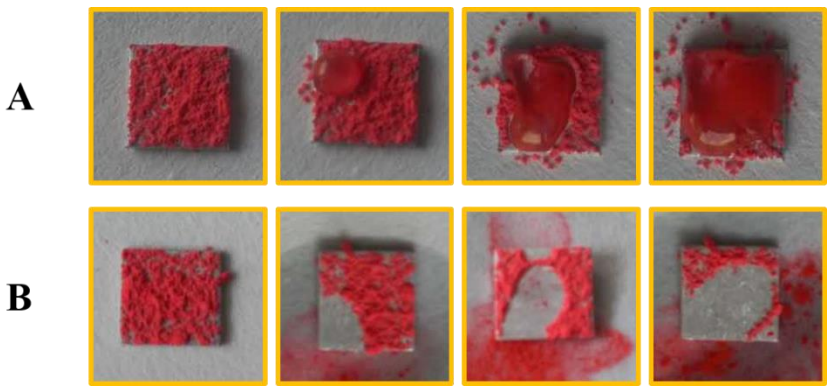


Figure 3. Self-cleaning property test: (A) bare Al substrate; (B) Ag SHS on Al substrate.

3.4. Stability

The stability of SHS is an important factor to determine the feasibility of the proposed method for the practical application. In our study, the stability of each SHS was evaluated by measuring the WCA after exposing to air in different period as shown in figure 4, and the error bar is 1°. We can see that the value of WCA of each sample is over 150° after 6 months, which had nearly no variation, indicating that the prepared SHSs display the good long-term stability in air.

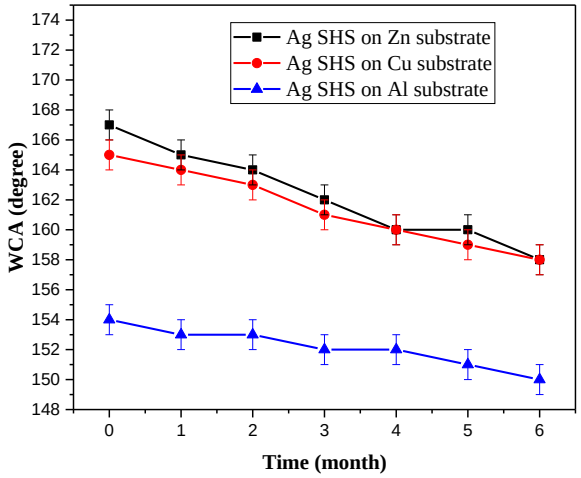


Figure 4. The WCAs of different samples after exposing to air in different period: (A) Ag SHS on Zn substrate; (B) Ag SHS on Cu substrate; (C) Ag SHS on Al substrate.

4. Conclusion

In this work, the facile approaches were developed for preparation the stable Ag superhydrophobic surfaces (SHSs) on zinc, copper and aluminium substrates. The water contact angle on each substrate could reach to 150° and the water sliding angle was less than 1°. The morphology and chemical composition of the surfaces were characterized using scanning electron microscopy (SEM) and X-ray diffraction pattern (XRD). The as-prepared three SHSs possessed the self-cleaning property and good stability, which had potential industrial applications.

Acknowledgements

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