



Superhydrophobic surfaces on diverse metals based on ultrafast sequential deposition of silver and stearic acid

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ARTICLE INFO

Article history:

Received 2 August 2014

Received in revised form

18 November 2014

Accepted 19 November 2014

Available online 27 November 2014

Keywords:

Superhydrophobicity

Galvanic replacement

Time-saving

Universality

ABSTRACT

In the presence of NaF, silver (Ag) was galvanically deposited onto aluminum (Al) substrate quickly (typically 10 s) from dilute aqueous AgNO₃ solution. Subsequent immersion into ethanolic solution of stearic acid (SA, for 30 s) rendered Al superhydrophobic. The deposition and morphological evolution of Ag were investigated in detail. It was found that NaF was indispensable to initiate the Ag galvanic deposition by dissolving the barrier oxide layer. Moreover, as reaction time prolonging, surface morphology and surface wettability varied synchronously. This strategy to fabricate superhydrophobic surface (coded as SHS) was also applicable to many other metals, such as Fe, Co and Mo with oxide passivation layer (NaF was needed) or Mg, Zn, Sn, Pb, and Cu with no apparent oxide passivation layer (NaF was not needed). In summary, the strategy to fabricate SHS based on Ag deposition and SA modification was quite impressive for its time-saving benefits and wide substrate applicability.

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1. Introduction

Lotus leaf exhibits excellent water repellency due to the synergistic effect of surface morphology (i.e., hierarchical rough structure) and surface chemistry (i.e., wax layer with ultra low surface energy) [1]. Learning from the lotus leaf, lots of artificial superhydrophobic surfaces (coded as SHS) have been fabricated on diverse substrates by two-step methods. Typically, surface morphology was firstly tailored by different techniques of anodization [2,3], electrodeposition [4], laser treating [5], electrospinning [6,7], chemical vapor deposition [8], sol-gel processing [9], etc. Then, surface was passivated by low-surface-energy molecules of fluoroalkyl-silane [2,3,10–12], fluoroalkyl mercaptan [4,13], poly(alkyl siloxane) [14], etc.

To fabricate SHS on aluminum (Al), which is an important material widely used in industrial production and our daily life, surface morphology was most conveniently tailored by solution-based methods. Many chemicals, such as HCl [15], NaOH [16], CuSO₄ [17], and even H₂O [18,19], were used to etch Al. However, these reported methods were time-consuming (Supplementary

Table S1). It was reported that the electroless galvanic deposition of dendritic Ag on copper could be finished quickly (tens of seconds) [20]. Inspired by this, we aim to develop a similar time-saving strategy for Al. However, AgNO₃ can not react with Al due to the barrier effect of Al₂O₃, which is supposed to be formed once the polished Al is immersed into aqueous AgNO₃ solution (Fig. 1 and Eq. (3)). Recently, it was reported that, the Al₂O₃ barrier layer could be dissolved by F⁻ [21,22]. So, herein, an aqueous solution of AgNO₃/NaF was used to facilitate the Ag quick deposition.

The other aim of this work is to develop a universal strategy to fabricate SHS on a wide range of metallic substrates. Although numerous strategies have been developed for different metals, this is still challenging. For metals of Mg, Zn, Fe, Sn, Pb, and Cu, the details of these reported strategies were summarized in Supplementary Table S1. It can be seen that the details for these strategies are quite different. In other words, it is difficult to develop a universal solution-based technique for so many metals. Despite such a big difference in the chemical composition and chemical reactivity of these metals, there is a common chemical property of these metals, i.e., the galvanic replacement reaction with AgNO₃. Taking advantage of the galvanic replacement reaction, rough Ag structures were deposited onto the metals listed in Table S1 and Co/Mo. After further surface passivation with stearic acid (SA), SHS on a wide range of metallic substrates could be obtained under the synergistic effect of rough structures of Ag and low surface energy of SA. This strategy to fabricate SHS based on sequential deposition

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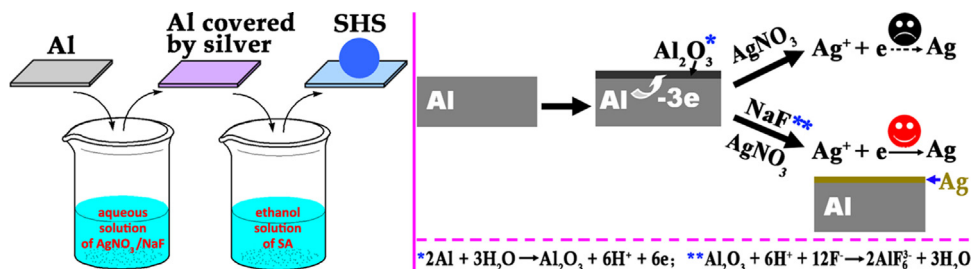


Fig. 1. The fabrication procedure for SHS based on replacement between AgNO_3 and Al as well as the possible reaction mechanism.

of Ag and SA was quite impressive for its time-saving benefits and wide substrate applicability.

2. Experimental details

2.1. Fabrication of SHS

To get rid of surface contamination, Al substrates were ground with abrasive paper and then ultrasonicated in acetone, ethanol as well as ultrapure water for 10 min, respectively. Subsequently, the Al substrates were immersed into an aqueous solution of AgNO_3/NaF with different concentration to facilitate the galvanic deposition of Ag. After rinsing with copious of water and drying with air stream, the substrates were transferred into an ethanolic solution of stearic acid (SA, 10 mM) for 30 s. Finally, the substrates were taken out and dried with air stream. The so-obtained samples after Ag deposition and SA passivation were coded as Al–Ag and Al–Ag–SA, respectively.

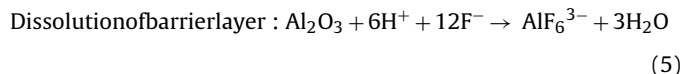
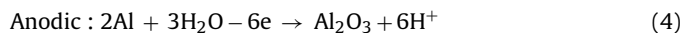
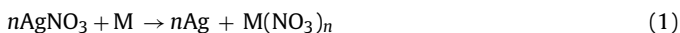
For Fe, Co, and Mo, the fabrication procedure was the same as Al. Specifically, polished metallic substrates were immersed into aqueous solution of AgNO_3 (10 mM)/NaF (0.1 M) for 15 s and subsequently in ethanolic solution of SA (10 mM) for 30 s. For other metals of Mg, Zn, Sn, Pb, and Cu, substrates were immersed into aqueous solution of AgNO_3 (30 mM) for 10 s and subsequently in ethanolic solution of SA (10 mM) for 30 s.

2.2. Characterization

The morphological microstructures were observed on scanning electron microscopy (SEM, FEI, Quanta200, USA; for Fe and Co) or field emission scanning electron microscope (FESEM, Nova NanoSEM, FEI, USA; for others) under vacuum environment and the samples were pre-sputtered with a thin palladium/gold film. Energy dispersive X-ray (EDX) spectra were used to analyze the composition of the samples. The chemical state of the surface species was characterized by X-ray photoelectron spectroscope (XPS, Physical Electronics, PHI-5702, USA). An optical contact angle meter (Easydrop, Krüss, Germany) with a computer-controlled liquid dispensing system and a motorized tilting stage was used to measure water contact angle (CA) and rolling-off angle (RA) at ambient temperature (20 °C) with 8 μL ultrapure water as probe liquid.

3. Results and discussions

Ag can be deposited on active metallic substrates (M) through galvanic replacement (Eq. (1)) and the concurrently occurring chemical reaction can be expressed by the following two half-cell reaction equations (Eqs. (2) and (3)) [22]:



However, for Al, insulating barrier layer of Al_2O_3 , which is supposed to be formed once the polished substrate is immersed into AgNO_3 solution (Eq. (4)), will prevent Ag^+ from being further reduced by Al (0). Therefore, Ag cannot be deposited (Fig. 1). To solve this problem, Gutés et al. used an uncommon and expensive reagent of AgF [21]. More recently, Ye et al. reported that the addition of NaF to AgNO_3 dilute aqueous solution (10 mM) could initiate the galvanic replacement quickly by dissolving Al_2O_3 (Eq. (5)) [22]. Taking advantage of such NaF-assisted Ag quick deposition, we aimed to develop an ultrafast strategy for SHS on Al substrate.

After immersed into an aqueous AgNO_3 (10 mM)/NaF (0.2 M) solution for a short while (few seconds), Al substrate was covered by Ag and the appearance of Al changed from gray to dark gray (Video S1 in supplementary data). As immersion time prolonging, the surface became darker and darker (Fig. 2a). The Al–Ag sample with an immersion time in AgNO_3 (10 mM)/NaF (0.2 M) for 10 s was investigated by EDX (Fig. 2c) and XPS (Fig. 2d) techniques. The so-deposited Ag was confirmed by the strong peaks of element Ag in EDX spectrum. Other weak peaks from Al substrate, adventitious carbon, and residual NaF were also observed. The XPS spectrum of Ag 3d with peaks centered at 368.3 eV ($3d_{5/2}$) and 374.3 eV ($3d_{3/2}$), which were close to reported values for Ag (0) in Ref. [22], also confirmed the successful deposition of metallic Ag. The Al–Ag sample was carefully observed by FE-SEM to show the surface morphological evolution (Fig. 2b). It was observed that nanoparticles (typical size was measured to be 79 nm and 95 nm) were sparsely deposited thereon to form microstructures. Moreover, some micro-grooves quite different from abrasive ones appeared (Fig. S1), which were probably due to the heterogeneous dissolution of Al_2O_3 by F^- (Eq. (4)). To estimate the effect of such micro-grooves on surface wettability, the Al–Ag sample was ultrasonicated to remove the deposited Ag and then modified with SA. CA for such sample was measured to be $137 \pm 3.4^\circ$, which was greater than that for abraded Al modified with SA ($129.8 \pm 2.1^\circ$). This suggested that the dissolving of barrier layer by NaF played a dual role in the SHS fabrication process, i.e., initiating the Ag deposition and roughening the surface structures. As immersion time prolonging from 5 s to 10 s (Fig. 2b), the dendritic microstructures became denser and the superhydrophobicity after SA passivated was enhanced (CA increased from 166.3° to 172.4° , RA decreased from 5° to 2°). Further prolonging the immersion time to 60 s, the Ag dendritic microstructures became much denser (even some micro-blocks were deposited) and the surface became compact; consequently the superhydrophobicity after SA passivation deteriorated (CA decreased to 164.0° , RA increased to 22°). For 600 s, some flat flakes and micro-balls were formed and the water droplet was firmly pinned on the surface even when the upside down.

The influence of concentration of NaF and AgNO_3 (abridged as [NaF] and [AgNO_3], respectively) on surface wettability of

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