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Reversible transition between superhydrophobicity and superhydrophilicity of a silver surface

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ABSTRACT

In the present work, superhydrophobic silver surface was prepared by immersing a copper plate in an aqueous solution of $AgNO_3$ for 20 min. The sample exhibits superhydrophilicity after dried at 150 °C for 30 min in an oven. The as-prepared silver surfaces exhibit contact angle (CA) larger than 160° and sliding angle (SA) lower than 5°. Neither low surface free energy (SFE) materials nor organic compounds were used during the producing process. It was suggested that the spontaneously adsorbed carbon contaminant with low SFE was very critical for the superhydrophobicity of silver surface during heat treatment. Additionally, the silver surface could be switched between superhydrophobicity and superhydrophilicity by alternating UV irradiation and heat treatment for many times. Our findings in this work might provide a simple route to rational control the spontaneously adsorbed carbon contaminant on solid surface to endow the metal or other solid surfaces with superhydrophobicity or superhydrophilicity.

1. Introduction

A surface is defined as superhydrophobic surfaces when it possesses very high contact angles (CA > 150°) and very low sliding angles (SA < 10°) [1]. Artificial superhydrophobic surfaces can be prepared by either roughing an intrinsic hydrophobic material (e.g., Teflon) or modifying a rough surface with low surface energy reagents [2]. Superhydrophobic surfaces based on metal substrates have received much attentions because of their several potential applications, such as anti-corrosion [3], fluidic drag reduction [4], anti-icing [5], and so on [6–8]. Generally speaking, pure metal surface is hydrophilic with high surface free energy (SFE) [9]. In the past few decades, the superhydrophobic metal surfaces were usually fabricated by creating rough microstructures first and followed by modifying the rough surface with long chain alkyl compounds, such as n-octadecanoic acid, dodecanethiol, heptadecafluoro-1,1,2,2,-tetrahydrodecyl)trichlorosilane [4,10,11]. For example, superhydro-phobic surface based on copper substrate was prepared by immersing the copper substrate into a mixed solution of $(NH_4)_2S_2O_8$ and NaOH, then the surface was modified with stearic acid [10]. Superhydrophobic surfaces based on Zinc or copper were prepared in the aqueous solution of $AgNO_3$ or $HAuCl_4$ and then modified it with $CF_3(CF_2)_7CH_2CH_2SH$ [11]. Superhydrophobic silver surface on glass was prepared via the silver mirror reaction while the modification with n-dodecanethiol could not be avoided [4]. However, the usage of low surface energy material has many limitations: such as expensive, dangerous for human being and the environment, and easy to peel off during normal use, which causes a decline of the superhydrophobicity. Therefore, it is meaningful to develop superhydrophobicity surface without using any low surface energy material.

In recent years, it has been reported that superhydrophobic pure metal surfaces, such as Ag, Au, Pt, Bi and Sn can be prepared by simple methods without the modification of long chain alkyl compounds [4,9, 12–15]. However, the interrelations between the superhydrophobicity of a metal surface and the surface adsorbed carbon contaminant have still remained unclear. For example, superhydrophobicity pure silver surfaces with surface flower-like microstructures were prepared via a facile immersion reaction without any modification [9]. They concluded that this unique morphology was responsible for the superhydrophobicity of the surface. In other words, the influence of carbon contaminant on the superhydrophobicity had not been taken into account. However, it is concluded by T. Smith that a clean metal surface is hydrophilic and a partial monolayer of carbonaceous contamination will make it hydrophobic [16]. In addition, superhydrophobicity pure metallic Sn surface was prepared via a displacement reaction between Zn substrate and $SnCl_2$ aqueous solution without needing surface modification [15]. The XPS spectrum clearly indicated the existence of carbon adsorption. However, the influence of carbon was still ignored. Only few literatures have verified that hydrocarbon molecules adsorbed spontaneously on solid surface was very critical in the superhydrophobicity, such as boron nitride nanotubes and graphene

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[17,18]. However, to the best of our knowledge, the influence of spontaneously adsorbed carbon contaminant on the superhydrophobicity of a silver surface has rarely been reported.

In this article, we investigate the interrelation between the superhydrophobicity of a silver surface and the spontaneously adsorbed carbon contaminant during heat treatment (HT). The silver surface was prepared by a simple chemical immersing method using aqueous solution of $AgNO_3$ (0.001 M) at room temperature. The spontaneously adsorbed carbon contaminant can lower the SFE of silver quickly and effectively during the HT process. After HT at 150 °C for 30 min, the silver surface exhibits superhydrophobicity. The carbon contaminant adsorption cannot be prevented because the volatile organic compounds (VOC) exist everywhere [19]. If the surface energy of a metal could be lowered by the spontaneously adsorbed carbon contaminant effectively at certain conditions, it might provide a novel, low-cost and green route to fabricate superhydrophobic metal surface without using any additional low surface energy material.

2. Experimental section

2.1. Materials

Copper foil (purity 99.9%) with thickness of 30 μm, silver nitrate ($AgNO_3$), hydrochloric acid (HCl) and ethanol were purchased from Shanghai Chemical Reagent (China). SiC sandpaper with a grade of 1000# was obtained from 3M Company.

2.2. Preparation

Copper substrates (25 mm × 25 mm) cut from the foil were first polished with sandpaper and then ultrasonically cleaned in ethanol, HCl (0.1 M) and deionized water respectively to remove the surface impurities. After that, the copper substrate were immersed in 50 mL aqueous solution of $AgNO_3$ (0.001 M) at room temperature. The color of the substrate changes to black gradually during the immersing process. After immersing, the sample was heated at 150 °C for about 30 min and then allowed to cool to room temperature.

2.3. Characteristics

Contact angle (CA) and sliding angle (SA) for water were measured using an optical contact angle measuring apparatus (Krüss DSA 100, Germany) with 4 μL of deionized water. The surface microtopographies were measured using a field emission scanning electron microscopy (FE-SEM, NanoSEM-450, FEI-Nova, America). The elemental analyses of the samples were performed on an X-ray energy-dispersive spectrometry (EDS, INCA 250, Oxford Ins). The X-ray diffraction (XRD) patterns were measured using an X-ray diffractometer (X'Pert Pro MPD, Philips, Netherlands). The chemical composition of the silver-modified sample surface was analyzed by X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd., UK) using Cu Kα radiation ($\lambda = 1.5418$ Å).

3. Results and discussion

Copper plates were immersed in a solution of $AgNO_3$ and left for different times. The FE-SEM images of these prepared samples are shown in Fig. 1. The initial copper substrate only exhibits scratches on its surface [Fig. 1(a)]. After immersed in $AgNO_3$ solution, the changes of the surface morphologies are obvious. When the immersion time is short (5 min), only small particles and few clusters were formed on the surface [Fig. 1(b)]. When the immersing time increases to 10 min, the clusters become bigger. However, only sparse clusters can be observed on the surface. Upon increasing the immersion time to 20 min, dense and uniform clusters throughout the surface of the substrate can be observed. In addition, a further increasing of the immersion time leads to the increment of both the size and the amount of the clusters [Fig. 1(e)]. Fig. 1(f) is the magnified FE-SEM image of Fig. 1(d). One can see that the clusters exhibit flower-like appearances, which are composed of many submicro-sized particles and/or slices. The initial copper substrate exhibits a CA of about 83.3° [see inset in Fig. 1(a)]. In addition, all the samples exhibit superhydrophobic after different immersion times from 5 min to 30 min. The as-prepared silver surface with an immersion time of 20 min [Fig. 1(d)] is selected for further characterization. The surface exhibits superhydrophobicity (CA is 165.5° and SA is 4.3°) without any post modification.

The XRD patterns of the copper substrates before and after immersion were showed in Fig. 2. The diffraction peaks at 43.1°, 50.4° and 74.0° can be attributed to the (111), (200) and (220) planes of face-centred cubic (FCC) copper (JCPDS No. 85-1326) [12]. The peaks at 38.1°, 44.3°, 64.5° and 77.5° can be attributed to the (111), (200), (220) and (311) planes of silver (FCC, JCPDS No. 04-0783) [4]. The peak at 36.4° can be attributed to the (111) plane of cuprous oxide (Cu_2O, JCPDS No. 5-667) [20]. It could be concluded that both metallic silver and Cu_2O are formed on the copper substrate after immersion. The related reaction between copper substrate and $AgNO_3$ aqueous solution could be expressed by the following chemical equations [11,12]:

$$Cu + Ag^{+} \rightarrow Ag + Cu^{2+} \tag{1}$$

$$Cu + Cu^{2} + + H_2O \rightarrow Cu_2O + 2H^{+}. \tag{2}$$

In this work, the effect of spontaneously adsorbed hydrocarbons on the surface superhydrophobicity of the sample was studied by XPS analysis. Note that the depth of detection of XPS is in the range from 1 to 10 nm [+20], it is very suitable for the analysis of chemical component and their concentration of superhydrophobic surfaces [20]. Fig. 3(a) indicates the survey spectrum of the superhydrophobic silver surface. It can be observed that peaks of elemental carbon, copper, silver and oxygen are exhibited in the XPS spectrum. Two main peaks at binding energies of 953.2 eV and 932.4 eV can be ascribed to the double peaks of Cu_2O [$Cu2p_{1/2}$ and $Cu2p_{3/2}$, see Fig. 3(b)] [20,21]. The binding energies of $Ag3d_{3/2}$ and $Ag3d_{5/2}$ occurred at 374.3 eV and 368.2 eV, separately, which can be ascribed to the metallic Ag [$Cu2p_{1/2}$ and $Cu2p_{3/2}$, see Fig. 3(c)] [9,22]. Fig. 3(d) shows that three peaks with binding energy at 284.4, 286.3 and 288.1 eV are corresponded to three different carbon groups, i.e., C—C/C═C/C—H (non-polar groups), C═O/C—O (polar groups), respectively. The C1s peak was deconvoluted and the obtained percentages of different C-based functional group (C═O, C—O and C═C/C—C/C—H) are 6.64%, 0.00% and 93.36%, respectively. The C—C/C═C/C—H non-polar groups are predominant among them, which possess low SFE [23–25]. Hence, XPS measurements confirm the existence of Ag, Cu_2O and spontaneously adsorbed carbon contaminant on the surface of superhydrophobic sample. The coarse surface microstructures [Fig. 1(d) and (f)] combined with the spontaneously adsorbed carbon contaminant on the surface with low SFE leads to the superhydrophobicity of the as-prepared silver surface.

It should be mentioned that the HT is a key factor to endow the silver surface with superhydrophobicity. Without HT, the silver surface after immersion is superhydrophilicity, with a CA of about 2.1° even it is naturally dried or dried with a hot-air blower. The silver surface remains its superhydrophilicity when stored at ambient condition for 1 month. However, after HT at 150 °C for 30 min and naturally cooled, the silver surface exhibits excellent superhydrophobicity (CA = 165.5° and SA = 4.3°) and long term stability for about 6 months. The surface morphology and chemical component of the silver surface after HT were also measured for comparison [see Figs. 4 and 5].

It was observed from the FE-SEM images [Figs. 1(e), (f) and 4(a) and (b)] that the surface microstructures of the silver surface before and after HT are very similar. In addition, the XPS survey spectrum and the high-resolution spectra of Cu2p, Ag 4f and C1s of the sample after HT [see Fig. 5] are also very similar to the sample before HT [see Fig. 3]. Therefore, the HT neither destroys the microstructures nor changes