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Novel, stable and durable superhydrophobic film on glass prepared by RF magnetron sputtering

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ABSTRACT

A novel and facile approach has been adopted to fabricate a nanostructured superhydrophobic (SHP) film on glass by radio frequency (RF) magnetron sputtering. The surface morphology, XRD pattern, chemical composition and wettability were analyzed by corresponding methods. It was found that the as-prepared SHP surface exhibited a prominent superhydrophobicity with a contact angle (CA) up to 168.9° and sliding angle less than 1°, which was mainly attributed to the low surface energy of hexadecyltrimethoxy silane and Al_2O_3-ZnO (mass ratio (Al/Zn) ≈ 1:1.2) nanofibers along with the presence of high proportions of micro/nano air pockets induced by a hierarchical composite network. Moreover, the as-prepared SHP surface demonstrated good stability under outdoor and ambient environment, and retained its superhydrophobicity even at severe temperatures as well as in strong corrosive surroundings.

1. Introduction

Inspired by the well-known lotus effect, various superhydrophobic (SHP) surfaces have been investigated for their potential applications in oil-water separation [1], self-healing [2], anti-corrosion [3] and anti-icing [4], etc. Based on the recognized process of constructing of rough mircostructures and modifying with low-surface-energy materials, many techniques have been proposed to synthesize SHP surface such as sol-gel [5], anodic oxidation [6], electrospinning [7] and physical vapor deposition (PVD) [8], etc. However, these methods are problematic because of certain requirements, such as large-area production, costly preparation, complicated process control and multistep procedures.

Magnetron sputtering has developed rapidly over the last decade, and it is one of the simplest and most effective methods available. Barshiilia et al. [9] prepared three different zinc oxide based coatings and discussed the effect of surface morphology on the adhesion, static and dynamic contact angle of water. Aytug et al. [10] combined magnetron sputtering with thermal processing and differential etching to obtain nanostructured SHP thin films. Perez et al. [11] utilized Al-x at.%Zn (x = 3, 6, 10, 16, 19) PVD coatings to study the influence of metallurgical states on the corrosion behavior, while neglecting how different surface morphology might affect the wettability. To the best of our knowledge, the literature [9,12–14] mainly explored ZnO SHP films obtained by sputtering zinc target, followed by annealing treatment. At present, studies on the Al_2O_3-ZnO SHP films fabricated through the analogous process still remain relatively scarce. Therefore, by selecting appropriate sputtering parameters, a fast and practical way to develop SHP coatings by RF magnetron sputtering may be designed [15].

Alumina is a ceramic material characterized by many advantages, such as good abrasive resistance, low dielectric constant, excellent anti-corrosion and high thermal stability, etc. All these properties make Al_2O_3 highly attractive for a wide range of technological applications. In this study, an Al-Zn film was easily fabricated by RF magnetron sputtering. Next, a novel Al_2O_3-ZnO hierarchical network film interwoven by nanofibers was obtained after annealing treatment. Finally, hexadecyltrimethoxy silane (HDTMS) was used to achieve superhydrophobicity of the film as the as-prepared SHP surface.

2. Experiments

2.1. Sample preparation

The glass slides were ultrasonically cleaned in distilled water followed by ethanol and subsequently dried. The films were prepared via RF magnetron sputtering of 50 wt% Al-Zn target (Deyang ONA New Materials Co. Ltd.; diameter, 61.5 mm; thickness, 5 mm). Sputtering was conducted in Ar plasma under a working pressure

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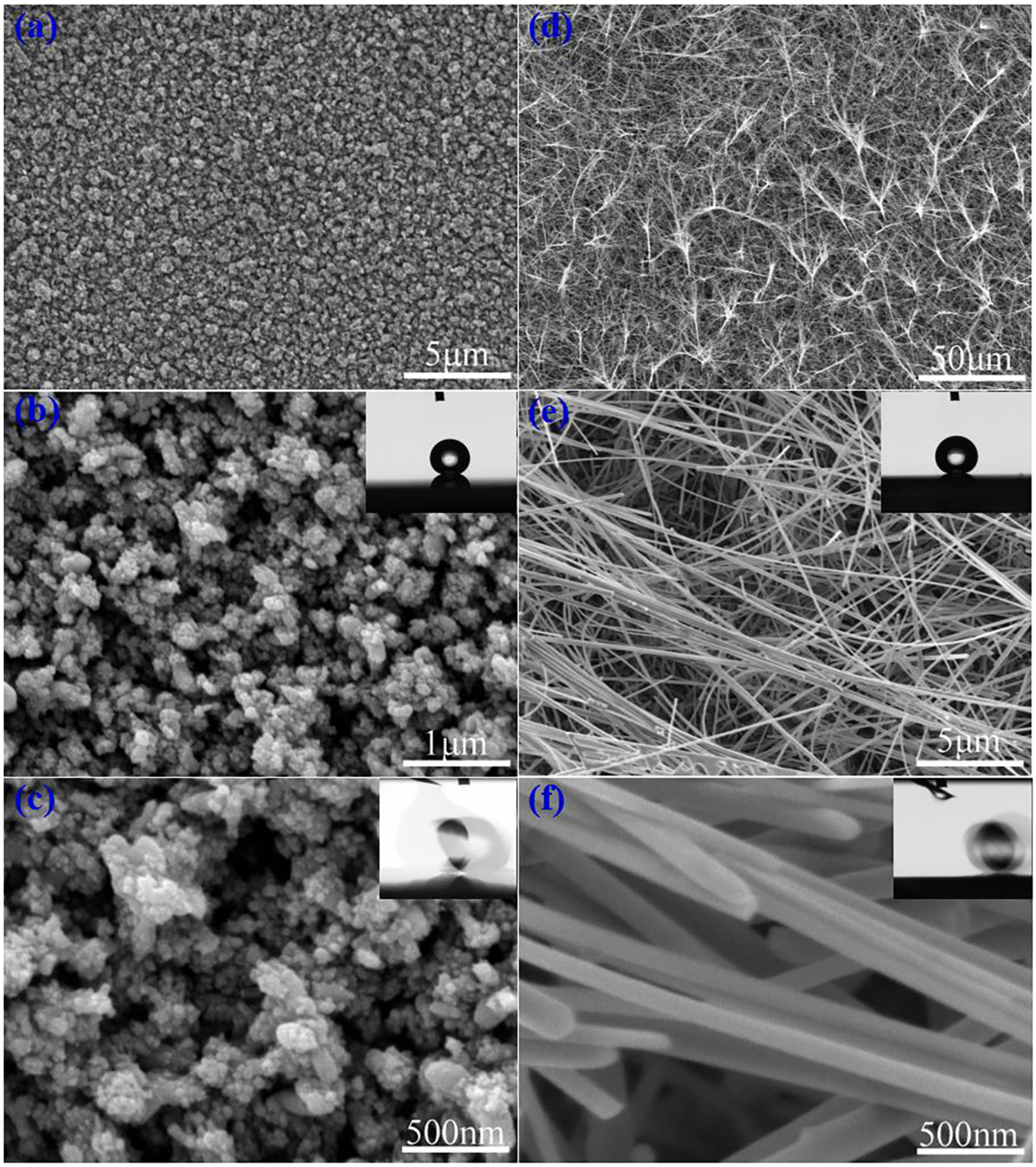

Fig. 1. SEM images of the Al-Zn SHP surface prepared by RF magnetron sputtering at (a) 5000×, (b) 25,000×, (c) 50,000×, and the as-prepared SHP surface at (d) 500×, (e) 5000×, (f) 50,000×.

of 1.0 Pa and a constant sputtering power at 100 W for 30 min with a fixed target-substrate distance of 10 cm. Thereafter, the films were oxidized in a muffle furnace from room temperature to 500 °C at a rate of 8 °C/min, maintained at 500 °C for 3 h and then naturally cooled down. The annealed sample was modified in 2 wt % HDTMS solution for 60 min and heated at 90 °C for 30 min.

2.2. Characterization

The SHP surface morphology was analyzed by field emission scanning electron microscope/energy dispersive spectrometer (FE-SEM/EDS; JEOL JSM-7800F, Japan). X-ray diffraction (XRD; Panalytical Empyrea, Netherlands) and Fourier-transform infrared spectrophotometer (FTIR; Nicolet iS5, USA) were performed to characterize the crystal structure and chemical composition, respectively. The wettability (average value from five different spots) of the samples was evaluated using an optical contact angle (CA) meter (Drop meter A-100, China) with a water volume of 10 μL at ambient temperature.

3. Results and discussion

3.1. Surface morphology

Fig. 1a–c show the typical SEM images of the SHP surfaces prepared by RF magnetron sputtering. Large numbers of hollow-like nanorods were randomly distributed on the surface, covered with nanoprotrusions ranged from 20 nm to 50 nm in size. However, after annealing treatment, a totally different morphology (Fig. 1d–f) was observed, i.e., bunches of nanofibers with diameters of about 150 nm, were found to be interwoven with each other to form a hierarchical composite network. These two micro/nano structures demonstrated that the surface roughness of the SHP surfaces was greatly enhanced in comparison with bare glass. Such a

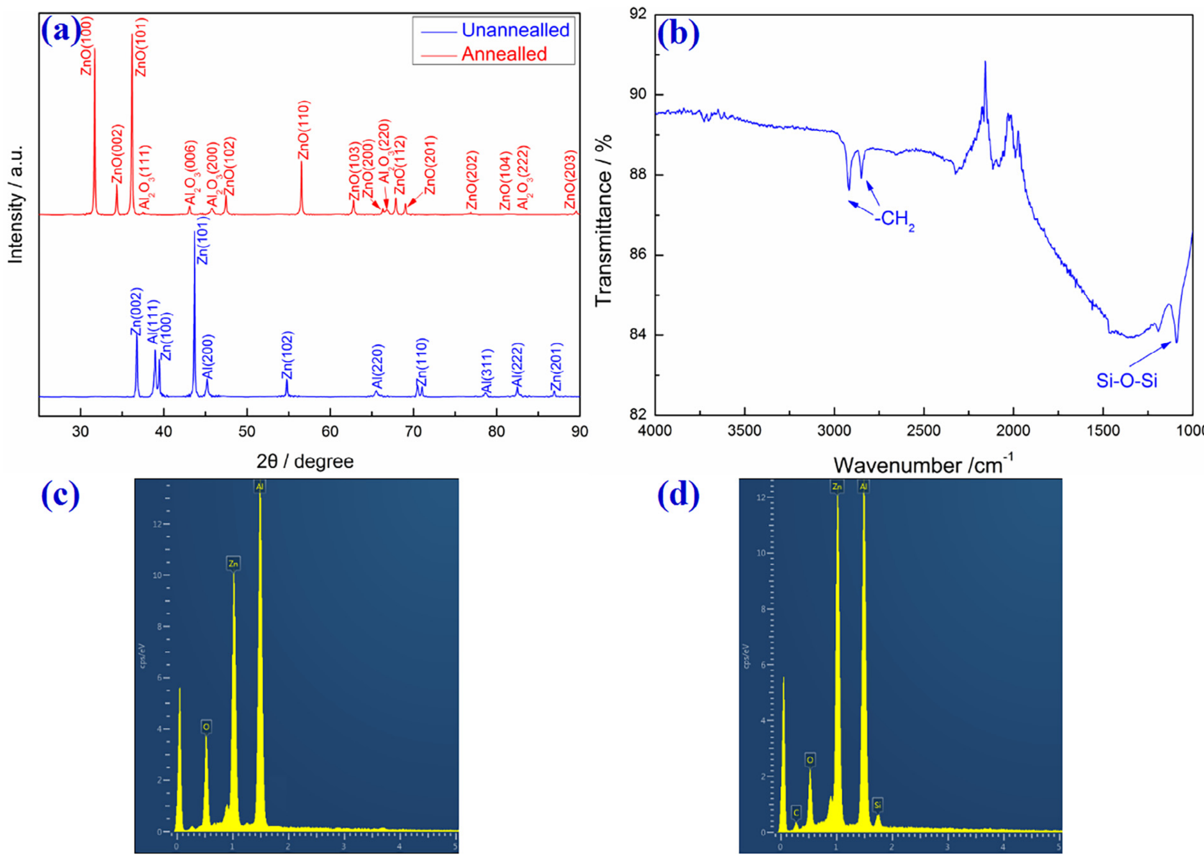

Fig. 2. The as-prepared SHP surface's (a) XRD patterns before and after annealing treatment, (b) FTIR spectra, and the EDS images (c) before and (d) after modification by HDTMS.

characteristic is beneficial to the absorption of large quantities of air and reduction of the actual solid-liquid contact area, leading to the construction of superhydrophobicity of the SHP surface.

3.2. Chemical composition

Fig. 2a shows the XRD patterns of the as-prepared SHP surface before and after annealing process. It could be found that the peaks centered at 2θ assigning to the planes of Al (JCPDS Card No. 04-0787) and Zn (JCPDS Card No. 04-0831) were converted into the ones of Al_2O_3 (JCPDS Card No. 10-0173) and ZnO (JCPDS Card No. 03-0888) after annealing treatment. As shown in Fig. 2b, the peaks around 2850 and 2918 cm^{-1} were attributed to the stretching vibration of the $–CH_2–$ and the peak observed at 1091 cm^{-1} was ascribed to the stretching vibration of Si-O bond along with the presence of C and Si (Fig. 2d). This result indicated the successful attachment of the silane molecule to the films through the hydrolysis of silane species with surface functional groups (Al-OH and Zn-OH) forming the self-assembled monolayer with low surface energy. The EDS spectrum of the surface presents peaks of Al-Zn-O without those of other elements (Fig. 2c), thereby suggesting the oxidation of the surface. The final Al/Zn mass ratio of the as-prepared SHP surface was 1:1.2, which could be determined on the basis of the EDS results.

3.3. Stability of SHP surface

In practical applications, glass products such as insulator, lamps and architectural materials are usually exposed to harsh conditions. Although low temperatures that cause the surface to frost and freeze might affect the function of modifiers and high temperatures allow the air to exit from micro/nano textures, the water CA of the as-prepared SHP surface remained higher than 160° even at −20 °C and 100 °C for 24 h (Fig. 3a). Fig. 3b shows the CA values of the as-prepared SHP surface when exposed to outdoor and ambient environment (15 ± 5 °C). After being placed outdoors for 40 days, the as-prepared surface still showed a high CA that reached 166.3 ± 1°. This result illustrated the good stability of the as-prepared surface in outdoor conditions. Furthermore, the glass surface may be exposed to high temperatures and corrosive liquids in special equipment. In this experiment, a 3.5 wt% NaCl solution and 90 °C temperature was used to accelerate the corrosion and degradation of the as-prepared SHP surface. In 2 h periods, the film was immersed in NaCl solution and then placed in an oven. After 12 h of treatment, the CA exhibited no distinct decrease (Fig. 3c), thereby indicating the capacity of the film to maintain its superhydrophobicity in high temperatures and corrosive liquids over a relatively long period.

4. Conclusion

The SHP Al_2O_3-ZnO film with a hierarchical network on glass was efficiently fabricated by RF magnetron sputtering followed by annealing treatment and then modification. The as-prepared SHP surface exhibited a CA of 168.9° and sliding angle smaller than 1°. The micro/nano structures can trap a large amount of air and reduce the liquid-solid interface to gain excellent superhydrophobicity. Besides, the as-prepared SHP film was stable under outdoor and ambient environments, and showed good durability against severe temperatures and strong corrosion.

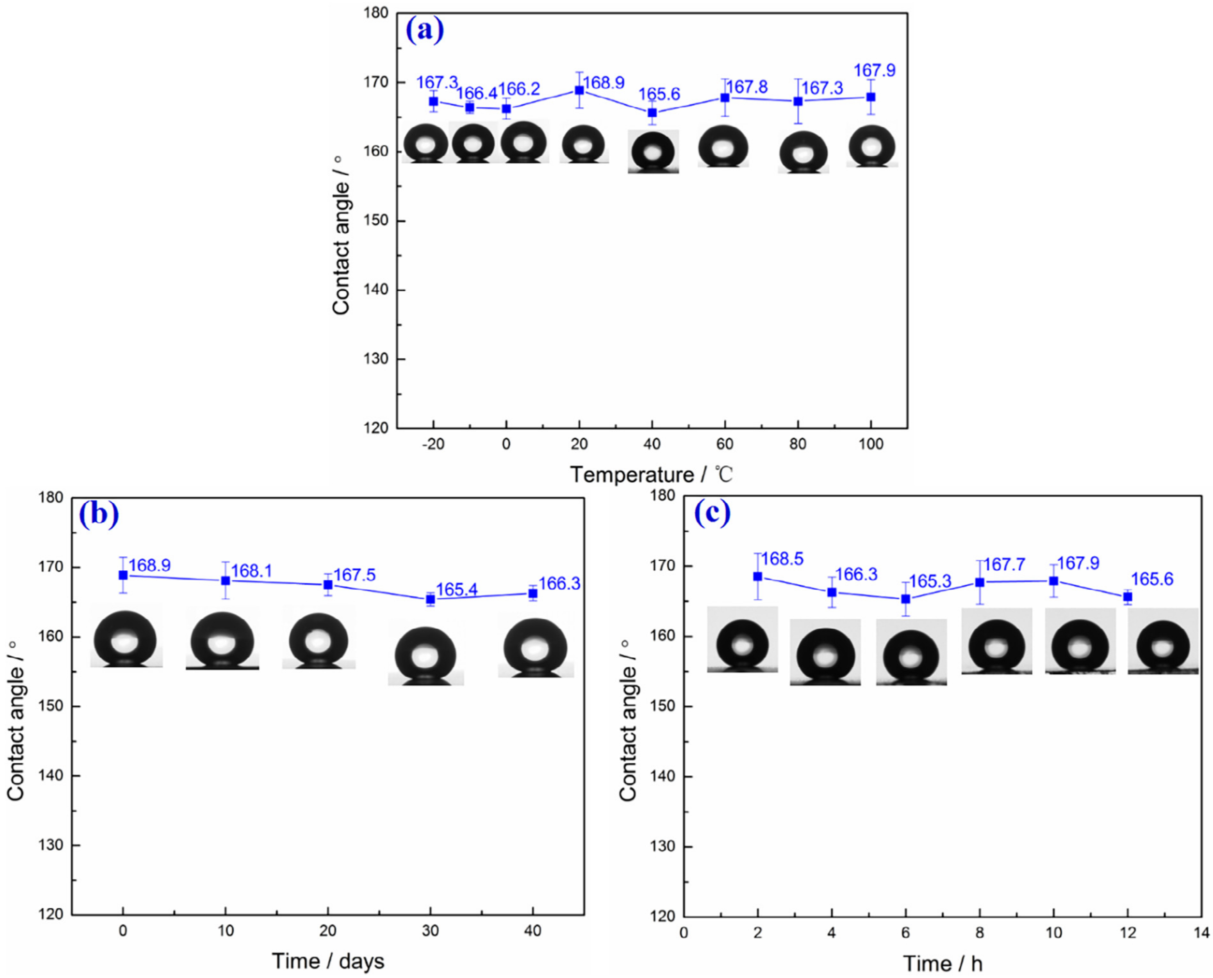

Fig. 3. Water CA on the as-prepared SHP surface (a) treated at each temperature for 24 h from −20 °C to 100 °C, (b) exposed outdoors from 0 to 40 days, and (c) after corrosive treatment from 2 h to 12 h.

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