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Formation process of a strong water-repellent alumina surface by the sol–gel method

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ABSTRACT

A novel strong water-repellent alumina thin film is fabricated by chemically adsorbing stearic acid (STA) layer onto the porous and roughened aluminum film coated with polyethyleneimine (PEI). The formation process and the structure of the strong water-repellent alumina film are investigated by means of contact angle measurement and atomic force microscope (AFM). Results show that the water contact angles for the alumina films increase with the increase of the immersion time in the boiling water, and meanwhile, the roughness of the alumina films increases with the dissolution of the boehmite in the boiling water. Finally, the strong water-repellent film with a high water contact angle of 139.1° is obtained when the alumina films have distinct roughened morphology with some papillary peaks and porous structure. Moreover, both the roughened structure and the hydrophobic materials of the STA endow the alumina films with the strong water-repellence.

1. Introduction

Wettability of the solid surface is a characteristic property of materials and depends on both the surface energy and the surface roughness [1,2]. A fundamental framework of this issue has been independently established by Wenzel and Cassie [3,4]. The difference between the two approaches is how a probe liquid contacts the surface. In Wenzel's approach, the liquid fully penetrates the surface grooves, so-called homogeneous wetting. On the other hand, Cassie proposed a notion of heterogeneous wetting, and the liquid does not get into the grooves because of trapped air. That is, the hills and valleys at the surface are in contact with the liquid and the air, respectively. Either way, increasing surface roughness makes the contact angle larger, although the contact angle must be higher than 90 °for Wenzel's approach.

Surface wettability is described by a contact angle, which is defined by Young's equation [5,6]. Since 1950s, much efforts have been made to increase the water contact angle, and many strong water-repellent surfaces have been successfully prepared since films with this surface can be used not only for resisting water and fog condensation [7], but also for self-cleaning (i.e., preventing contamination) [8–10]. Moreover, their applications have been extended to some new fields, such as biocompatibility, lubricity and durability of materials [11,12]. For a given system, there are two basic approaches to increase the contact angle. One is to change the surface chemistry that can lower the surface energy sufficiently, which is generally referred to as the chemical method. The other is to increase the surface roughness so as to increase the true or effective surface area resulting in the increase in nominal surface energy which is known as the geometrical method. For the formation of strong water-repellent films or coatings, modification of surface chemistry is always combined with surface roughness enhancement. For example, Schlenoff et al. [13] prepared hydrophobic and strong water-repellent multilayer thin films from perfluorinated polyelectrolytes combining a roughening step by inserting a nanorod; Watanabe and coworkers [14] fabricated transparent superhydrophobic boehmite and silica films by the use of a sublimable pore-forming material to provide roughness on film surface and then coated with fluoroalkylsilane; Xiao et al. [15] prepared the ultrahydrophobic surface based on the roughening the aluminum plates in the boiling water and a stearic acid adsorbed layer; Tadanaga and coworkers [16] reported that super water-repellent films can be fabricated on soda lime glass plates modified with fluoroalkyltrimethoxysilane, etc.

Herein, we report the formation and characterization of a novel strong water-repellent alumina thin film, which is fabricated by chemically adsorbing stearic acid (STA) layer onto the porous and roughened aluminum thin film coated with polyethyleneimine (PEI). Various surface roughness and morphology are achieved by careful control of the treatment time in the boiling water and proper chemical modification. The relationship between the contact angle, surface roughness and surface chemistry is discussed in detail.

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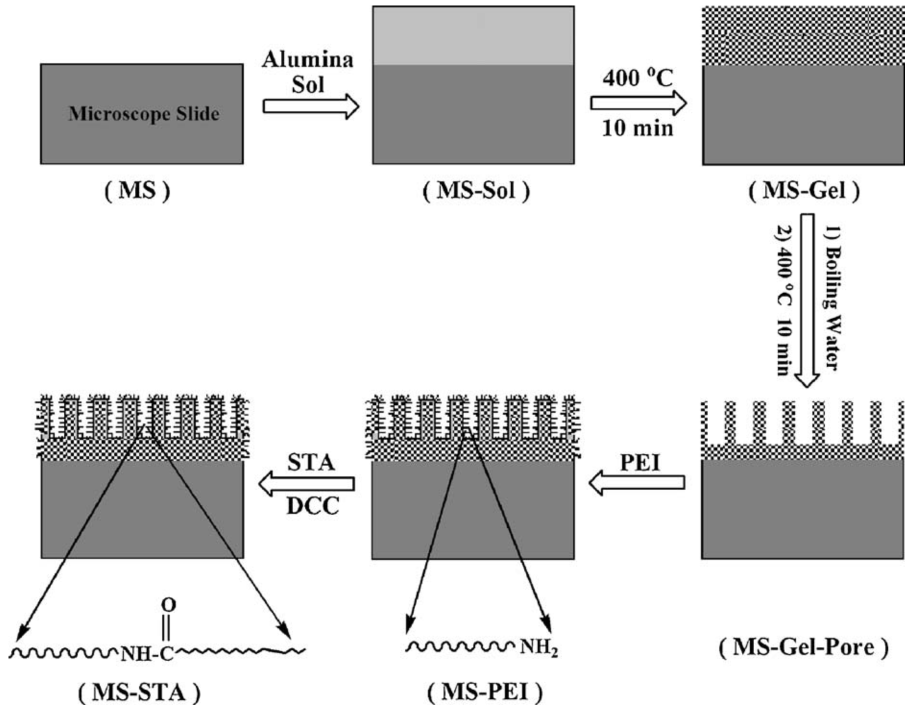

Scheme 1. The preparation procedure of the strong water-repellent alumina surface.

2. Material and methods

2.1. Materials

Aluminum tri-sec-butoxide [Al(O-sec-Bu)$_3$] and Polyethyleneimine (PEI, M_n: 10,000 g/mol, M_w: 25,000 g/mol, 30 wt% solution in water) were obtained from Aldrich and used as received. Isopropyl alcohol (i-PrOH), ethyl acetoacetate (EAcAc), stearic aicd (STA), and *N*,*N*′-dicyclohexylcarbodiimide (DCC) were all analytical purity and purchased from Sinopharm Group Chemical Reagent Co., Ltd. Acetone and *n*-hexane, etc., were from Tianjin Benchmark Chemical Reagent Co., Ltd. (China). Microscope slide (25.4 mm × 76.2 mm × 1.2 mm) was used as the substrate for growth of alumina films and cleaned sequentially in acetone and distilled water under ultrasonication before use.

2.2. Preparation of the alumina sol

The alumina sol was prepared via the hydrolysis and condensation of Al(O-sec-Bu)$_3$ in presence of i-PrOH, EAcAc, and water, and the preparation procedure was described as follows: first, 7.4 g of Al(O-sec-Bu)$_3$ and 18.0 g of i-PrOH were charged into a 250 mL of flask and stirred at room temperature for 1 h. Secondly, 3.9 g of EAcAc was added to the solution as a chelating agent and the solution was stirred for 3 h. Finally, the mixture of 2.2 g of distilled water and 18.0 g of i-PrOH was then carefully added to the solution with a drop funnel for Al(O-sec-Bu)$_3$ hydrolysis.

2.3. Fabrication of the porous alumina gel films

The alumina sol prepared above was used as a coating solution and the coating was carried out on the cleaned microscope slides (MS) with dipping-withdrawing method at a speed of 2 mm/s. The coating films obtained were kept at 50 °C for 5 h before they were heat-treated at 400 °C for 10 min to get porous alumina gel films. Then the porous alumina gel films were immersed in boiling water for 0–10 min. After being dried, the alumina films were heat-treated again at 400 °C for another 10 min.

2.4. Modification of the alumina gel films

In our study, PEI was used as a cation polymer to adsorb onto the surface of as-prepared porous alumina gel films since PEI can be easily adsorbed onto any hydroxylated solid surfaces through hydrogen bonds and Van der Waals forces [17]. Then STA layer was chemically adsorbed through the reaction between the carboxylic group in STA molecules and the amine groups in PEI. The detailed preparation process is described as follows: a thin layer of PEI was first formed by immersing the microscope slides covered alumina thin films into a dilute aqueous solution of PEI (0.2 wt%) at room temperature for 20 min. After rinsing with distilled water thoroughly, the resulting PEI-coated alumina substrate was dried at 40 °C under vacuum for 12 h. Then the PEI-coated alumina substrate was put into a dilute solution of STA and DCC mixture in *n*-hexane for 24 h (concentration of STA and DCC are both 3 mM). DCC was used here as dehydration reagent for the reaction of STA and PEI. At the end, the samples were washed sequentially with *n*-hexane, acetone and distilled water in order to get rid of the physisorbed impurities. Thereupon, a novel strong water-repellent alumina thin film was obtained. The schematic process for preparation of the strong water-repellent alumina surface is described in Scheme 1.

2.5. Surface wettability measurements

The wettability was evaluated by the water contact angle measurement of the as-prepared films, and the contact angles were measured with the hemisphere method [18]. The schematic principle of the method is shown in Fig. 1 and the contact angle can be calculated according to the Eq. (1).

$$\sin\theta = \frac{2hr}{h^2 + r^2} \quad \text{or} \quad \tan\frac{\theta}{2} = \frac{h}{r} \tag{1}$$

where θ is the contact angle while h and r are the height of the liquid drop and the radius of underside circle, respectively.