Applied Surface Science 324 (2015) 563–568

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Water-collecting behavior of nanostructured surfaces with special wettability

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ARTICLE INFO

Article history:
Received 16 July 2014
Received in revised form 13 October 2014
Accepted 13 October 2014
Available online 1 November 2014

Keywords:
Water harvesting
Wetting anisotropy
Textured surface
Inclination angle

ABSTRACT

Dew is commonly formed even in dry regions, and we examined the suitability of surfaces with superhydrophilic patterns on a superhydrophobic background as a dew-harvesting system. Nanostructured surfaces with mixed wettability were fabricated by ZnO and TiO_2 nanorods. The condensation properties were investigated by environmental scanning electron microscopy (ESEM), and the water-collecting function of the patterned surfaces in an artificial environment was confirmed. Condensation and water-collecting behavior were evaluated as a function of surface inclination angle and pattern shape. We examined the collecting efficiency among the different wettabilities at various inclination angles and observed the condensation behavior for various superhydrophilic shapes.

1. Introduction

In nature, many living things possess unique structures that exhibit different surface wettabilities depending on their habitats [1–4]. In arid regions, where access to water is difficult, many organisms use their functional surfaces to obtain water from the atmospheric air. For example, the skin of several lizard species is made of a superhydrophilic surface with a honeycomb structure. Moisture in the air is absorbed through their skin and the collected water is transported into their mouth by a capillary network [2,3]. Certain cacti possess conical spines and trichomes with hierarchical grooves. Through the Laplace pressure gradient, water droplets from air are efficiently collected and transported to the absorption region [4]. This process of using water from the air is known as water harvesting. Parker and Lawrence investigated the use of water harvesting by the beetle *Stenocara gracilipes*, which is found in the Namib Desert [5]. They reported that *Stenocara* beetles have hydrophobic hemispherical elytra with wax-free hydrophilic bumps. The beetles have received much attention since then, and many researchers have investigated patterned wettability in an effort to mimic this water-collecting capability [6–12]. However, several studies have shown that the beetles possess no hydrophilic regions. Although hydrophilic regions have been found to be absent in the beetles, many researchers have continued to investigate the relationship between hydrophilic and hydrophobic regions on condensation behavior via wettability [13–16]. For example, Lee et al. [13] studied condensation and collection rates under different wettability conditions; they also investigated the effect of the shape of the draining grooves. They reported that a superhydrophilic surface collected most of the water and a thin drainage path in the lower portion of the condensation substrate enhanced the water-collection efficiency. They concluded the superhydrophilic-patterned superhydrophobic surface did not fare better than a hydrophilic surface. However, optimal design geometry of the surface was identified through the experiments. Although numerous approaches for collecting water have been taken, experimental investigations of the relationship between the angle of inclination and the water-collecting ability needed for application in the real world are rare. Therefore, we investigated the water-collecting behavior of surfaces with varying wettabilities at various tilting angles and pattern shapes.

In this study, superhydrophilic patterns on a superhydrophobic surface using one-dimensional nanorods were fabricated. Among the metal oxides, TiO_2 [17,18] nanorods were fabricated to provide a superhydrophobic background. TiO_2 is capable of forming a large number of hydroxyl radicals on surfaces, thus facilitating reactions with self-assembled monolayers, and nanorods, which have high roughness, are easily fabricated. ZnO nanorods [19,20] were used to create the superhydrophilic pattern. ZnO nanorods with no treatment show superhydrophilic properties, and the height of the rods strengthens the pinning effect of the droplets. In order to apply

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http://dx.doi.org/10.1016/j.apsusc.2014.10.061
0169-4332/

the results to real walls, roofs, or sloping areas, we performed the experiments by inclining the samples at varying angles, and we confirmed the differences in behavior with significant wettability. This study can contribute towards the development of artificial water-harvesting products [21], open-air microchanneled devices [22], and patterning templates [23].

2. Material and methods

The overall fabrication process for patterned surfaces with dissimilar wetting properties is shown in Fig. 1. In order to create a superhydrophobic background, TiO_2 nanorods synthesized using the hydrothermal method were used. A self-assembled monolayer (SAM) with low surface energy was then coated on the substrate. Many studies have been conducted on SAM layers on oxide surfaces with various terminal groups such as octadecyl groups [24–26], phenyl groups [27], amino groups [28], and fluorinated groups [29]. Among them, we used a fluorinated SAM for the superhydrophobic surface because it has a relatively lower surface energy than a non-fluorinated SAM [30]. To create an array with a superhydrophilic pattern, ZnO nanorods were selectively grown by the hydrothermal method.

2.1. Fabrication of superhydrophobic TiO_2 nanorod background

A solution of TiO_2 was spin coated onto a silicon wafer as the seed layer. The substrate was prebaked on a 200 °C hot plate for 20 min. After prebaking, the substrate was annealed in a tube furnace for crystallization; the annealing temperature was maintained at 600 °C for 1 h. Then, TiO_2 nanorods were grown on the crystalline TiO_2 thin film by the hydrothermal method. In order to prepare the nutrition solution, distilled water (DI water, 30 mL) and hydrochloride (30 mL, 37%) were mixed in a Teflon-lined autoclave with stirring, and titanium butoxide (1 mL, 97%) was then added carefully to the solution. The substrate with the TiO_2 thin film was placed in the autoclave and heated at 120 °C for 2 h. After hydrothermal growth, the substrate was rinsed using DI water and dried by blowing with N_2. In order to reduce the surface energy, a fluroalkylsilane-based SAM was coated onto the TiO_2 nanorods.

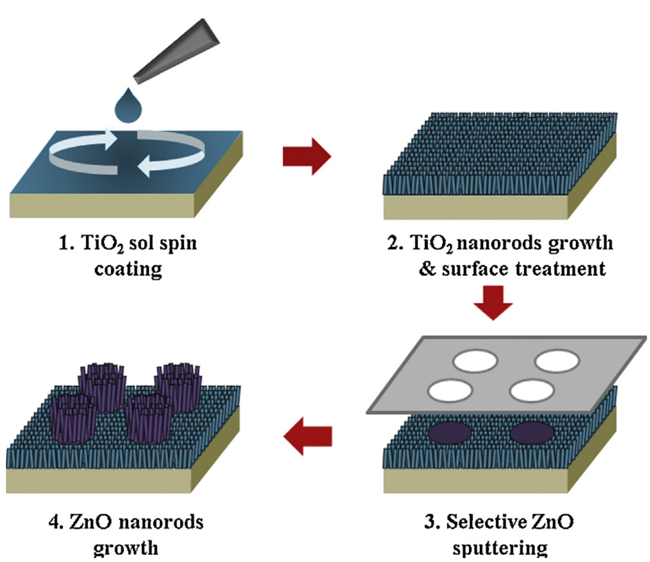

Fig. 1. (Color online) Schematic illustration of the fabrication of a superhydrophilic ZnO nanorod array on superhydrophobic TiO_2 nanorods.

A heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane (HDFS) solution was diluted in *n*-hexane at a concentration of 0.1 wt%. The sample was dipped in this solution for 10 min with magnetic stirring and then rinsed with DI water. Subsequently, the silane head groups of HDFS react with the hydroxyl group on the nanorods, hydrolyzing the nanorods and forming covalent bonds [29].

2.2. Fabrication of superhydrophilic ZnO nanorod array

Four different shadow masks – dot, line, mesh, and branch types – were used to fabricate four different ZnO nanorod array patterns. The substrate was loaded into the RF sputtering-system in order to deposit the ZnO seed layer. A shadow mask was used to selectively deposit ZnO. The sputtering process was operated at 50 W for 30 min. A nutrition solution was prepared for the growth: zinc nitride hexahydrate [$Zn(NO_3)·6H_2O$, 90 mM] and sodium hydroxide (NaOH, 1 mM) were added to DI water and stirred at 50 °C. Then, the ZnO-deposited substrate was immersed into the solution for 2 h. After selective ZnO nanorod growth, the substrate was cleansed using DI water.

Fig. 2(a) shows SEM (S-4300, Hitachi) micrographs of the patterned growth of the ZnO nanorod array on the TiO_2 nanorods. The ZnO nanorods were only grown inside a circular pattern with a diameter of 500 μm. Although the TiO_2 surface was covered with chemically inert SAMs, the ZnO seed layer deposited was strong enough to withstand processing using the hydrothermal method. Figs. 2(b) and (c) exhibit high-magnification images of Fig. 2(a). Fig. 2(b) shows the ZnO nanorod array inside the circular pattern, and Fig. 2(c) shows the TiO_2 nanorod array outside the circular pattern. Fig. 2(d) shows the cross-sectional view of Fig. 2(b). As shown in Fig. 2(d), ZnO nanorods with lengths of 1 μm were grown on TiO_2 nanorods with lengths of 500 nm.

3. Results and discussion

Table 1 shows the shadow mask specifications for ZnO nanorod patterning. The ratios of superhydrophilic to superhydrophobic regions were fixed at 0.195.

Table 2 shows the contact-angle measurements of the surfaces used in this work. Static contact angles for 10 μL of DI water on the horizontal surfaces were obtained. The critical advancing contact angles were measured by increasing the volume of the droplet at a rate of 0.05 μL/s using a syringe needle. The droplet images were captured before the contact line started to move, and then the angle between the solid surfaces and the tangential lines of the droplets were measured. The receding contact angles were also measured by decreasing the volume of the droplet in the reverse manner as the advancing contact angle. Each sample was measured three times and the values were averaged to obtain the final value. The intrinsic ZnO nanorod array exhibited very low contact angles; the static contact angle was nearly zero, indicating that the ZnO nanorod array possessed a superhydrophilic surface because of the high surface energy and roughness factor. On the other hand, the SAM-coated TiO_2 nanorod array exhibited a static contact angle of 161°, which indicates superhydrophobicity. The contact-angle hysteresis was small, indicating that the adhering force from the surface was very low. As compared to the superhydrophobic background, the adhesive forces of the four different types of superhydrophilic-patterned surfaces increased as determined from the contact-angle hysteresis.

In-situ water condensation on the superhydrophilic ZnO nanorod arrays on the superhydrophobic TiO_2 nanorod surfaces was also investigated using environmental field emission scanning