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An effective route for transparent and superhydrophobic coating with high mechanical stability

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ABSTRACT

Superhydrophobic surfaces possess incredibly useful properties in terms of repelling water and dirt. Yet, the transparency and mechanical durability are still the challenges to expand superhydrophobic coating to wider applications. In this paper, we introduce an effective and simple route to fabricate transparent & superhydrophobic coating with an excellent mechanical stability. The optical and wearing characterization shows that, by the surface coating of fluoridated vertical ZnO nanorods, high relative-transparency over 99% (compared with bare glass) and excellent endurance over sand abrasion are achieved, while maintaining excellent superhydrophobocity with over 160° in contact angle and less than 5° in sliding angle. The hydrophobicity coating by fluoride treated vertical ZnO nanorods can be also adaptive to conformal coating on micropatterned surfaces, i.e., microlens arrays, showing a promising superhydrophobicity and transparency while keeping the exactly lens profile. The robust superhydrophobic treatment while maintaining the transparence can find applications in various fields.

1. Introduction

Many surfaces in nature are superhydrophobic, e.g. lotus leaves [1]. Their surface morphology inspired the development of a number of artificial superhydrophobic surfaces [2,3], opening many applications in industrial and biological processes [4–9]. The primary objective to bio-mimic a superhydrophobic self-clean surface is to produce a desirable surface roughness with reduced surface energy. Smooth surfaces can have an intrinsic contact angle only up to about 120° [10,11]. Superhydrophobicity—contact angle over 150°—can be achieved by roughening a hydrophobic surface to establish a stable Cassie state, i.e. a state where the grooves of the surface pattern are not wetted by water [11]. In this instance, the mechanical stability of the microscopic surface topography that is essential for very large contact angles is greatly important, which hampers the practicality of non-wetting surfaces. Many recent studies [12–15] use roughness at two length scales to ensure that a stable Cassie state remains even after some surface features are worn away. Such morphology involves robust microscale bumps that provide protection to a more fragile nanoscale roughness that is superimposed on the larger pattern. However, surface roughness has been reported to compromise the optical transmissivity due to scattering in the optical wavelengths [16]. For the applications on optical lens, it is desirable to meet both the requirements of mechanical robust and the optical transmissivity. In addition, various optical components involve a micropatterned surface, so it is desirable to achieve conformal coating on the designed nonplanar surface. In this paper, a simple route to prepare high transparency superhydrophobic coating with a robust mechanical durability is introduced, which can be adopted to both planar and curved surfaces.

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2. Experimental details

For lotus leaves, it is well known that, a wax-like material with surface energies much lower than water lies on a rough surface consisting of micro- and nanostructures, which is the origin of its superhydrophobicity. To bio-mimic its structures and water repellant property, in this paper, ZnO nanorods were prepared on the pristine surface, and then followed by a fluoride treatment to for low surface energy.

In this paper, the ZnO nanorods were prepared by a conventional hydrothermal process to obtain various morphology and vertical nanorods. The ZnO seed layer (about 30 nm) is prepared by radio frequency magnetron sputtering with a ZnO target, at 150 W and 20 sccm flow of Ar for 9 min. After seed layer preparation, ZnO nanorod arrays are synthesized at 90 °C, by zinc nitrate hexahydrate ($Zn(NO_3)_2{\bullet}6H_2O$, 25 mM), hexamethylenetetramine (25 mM), and deionized water (100 ml), similar to previous studies [18]. Scanning electron microscope (SEM, SU-8010, Hitachi, Japan, operated at 30 kV) and X-ray diffraction (XRD, PIGAKV XRD-RINT 2000, Cu Kα_1 source) are employed to characterized the morphology and crystalline of the prepared ZnO nanorods. The fluoride treatment was done in an inductively coupled plasma

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system (ICP-180, Oxford Plasma, UK) in a C_4F_8 environment. The contact angle is measured by OCA20 (Dataphysics, German).

For the transmittance measurement, a UV–Visible-NIR spectrophotometer (UV-3600, Shimadzu) was employed. In order to evaluate the mechanical stability of coatings in outdoor environment, a self-made sand abrasion setup was used to simulate the common outdoor environment. To further evaluate the wear life of the prepared coating, a pin-on-disk tribometer was employed (the scheme of the tribometer is shown in Fig. 4.) in room temperature and humidity of 45%. In the tribotest, the rigid Si_3N_4 ball with radius (R) of 3.17 mm was chosen as the counter ball, and the disk of the prepared coating was fixed on the sample table. A normal load of 2 N was applied during the tribotest. The details of the tribotest system can be found in reference [21].

To evaluate the conformal coating ability, array of microlens, 40 μm in diameter and 20 μm in height, which was prepared by a conventional thermal reflow process [17], was decorated by the presented hydrophobicity coating, and then its imaging ability and hydrophobicity were characterized.

3. Results and discussion

3.1. Nanorod characterization and the wetting property of the coating

Fig. 1 shows the morphology and XRD pattern of the as-prepared ZnO nanorods. The as-grown ZnO nanorods are highly dense and vertically aligned to the substrate (Fig. 1(a)). The diameter of the nanorods can be tuned from 60 nm to 400 nm, dependent on the growth process, and the length is determined by the growth time. The growth feature is similar to the findings by others [18]. From the XRD pattern (Fig. 1(b)) of the as-grown ZnO nanorods, it indicates the hexagonal growth of ZnO rods, and "preferred to the (002) orientation (c-axis).

For the surface coating by pristine ZnO nanorods, the contact angle dramatically depends on the geometry of ZnO nanorods, as Fig. 1(c) shows. It is found that, (a) for the ZnO nanorods at same length, it gets less hydrophilic when the diameter is larger; (b) for the ZnO nanorods at the same diameter, it also gets less hydrophilic when length is larger. The rods geometry dependence of the contact angle can be explained by the classical Cassie–Baxter model, which is described by Eq. (1):

$$\cos\theta^* = f_1 \cos\theta - f_2 \tag{1}$$

where f_2 is the fraction of air spaces (open area) and $f_1 = 1 - f_2$ is the fraction of water occupation, θ is the contact angle on ideal smooth surface, named as ideal contact angle, and θ^* is the apparent contact angle on a fractional surface.

In our case, because of the high density of ZnO nanorods, water cannot penetrate the surface structures to replace air; thus, air pocket forms with the measurement of the contact angle. For ZnO rods at the same length, a larger diameter induces smaller gaps between the rods, which is adverse to the replacement of air and results in a larger f_2; therefore, the apparent contact angle θ^* increases. For ZnO rods at the same diameter, longer rods induce more traps of air, which also result in a larger f_2, so does θ^*.

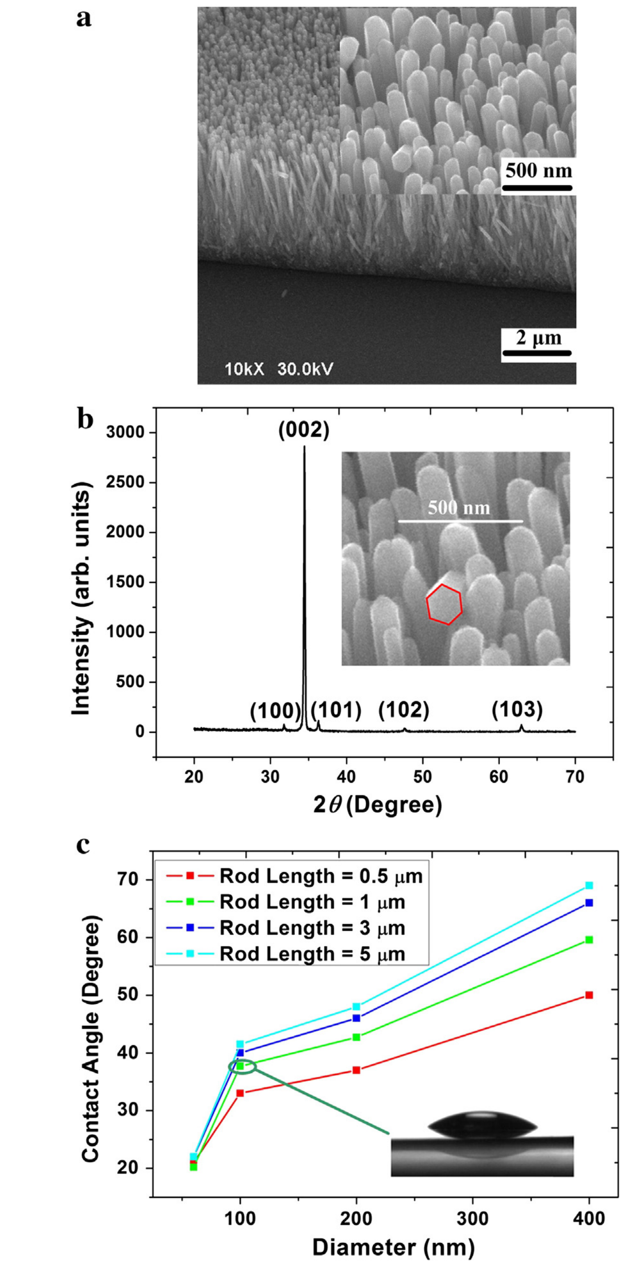

Fig. 1. Characterization of the prepared ZnO nanostructures (a) SEM image: 100 nm in diameter and 5 μm in length; (b) XRD for crystal orientation; and (c) the contact angle of the ZnO nanostructure before fluoride treatment, and the inset is the contact angle for ZnO rod coating (the rod is 100 nm in diameter and 1 μm in length), about 36°.

3.2. Low surface energy treatment and its superhydrophobicity

Although the as-prepared coating of ZnO nanorods is hydrophilic, it can be fluoridated to be superhydrophobic preferable for self-cleaning. Surface texture is an important and effective method to achieve superhydrophobicity [19]. As Fig. 1(a) shows, the morphology of ZnO rods supplies a perfect textured surface for superhydrophobicity. By C_4F_8 plasma treatment to introduce CF_n, the coating of ZnO nanorods can obtain superhydrophobicity, with a contact angle up to 160° and a sliding angle less than 5°, as Fig. 2(a) shows. Compared to the contact angles before C_4F_8 plasma treatment (shown in Fig. 1(c)), it can be found that, in our case, the coating gets more hydrophobic (larger θ^*) after the treatment of C_4F_8 plasma if it is more hydrophilic (smaller θ^*) before treatment. In previous studies, it is well known that the roughness of a hydrophobic solid can enhance its hydrophobicity [19] in our case, however, the roughness seems not enhance but hinder the improvement of the hydrophobic. Taking the C_4F_8 treated ZnO rods at same diameter for example, it is obvious that, longer rods induce higher roughness, thus suppose to induce larger apparent contact angle θ^*, which is opposite to our experimental results shown in Fig. 2(a). This may attribute to the process of C_4F_8 treatment. The treatment was employed in the ICP chamber by C_4F_8 plasma exploiting, introducing CF_n grafted on the ZnO rods [20]. Similar to sputtering deposition, a shadow effect also exists during the CF_n introduction on ZnO rods, especially when the rods have a large diameter or high density. The shadow effect induces inhomogeneous CF_n coating along the rods, e.g., the bottom and the sidewall

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