



Facile Fabrication of ZnO-Nanorods-Array Superhydrophobic Film Modified with Stearic Acid†

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Biomimetic superhydrophobic surfaces are attracting more and more research attention due to their potential application as self-cleaning materials. However, the complicated procedure, high cost and instability of most superhydrophobic surfaces significantly limited their applications. In this work, we report a convenient one-step route to obtain a large scale of ZnO-nanorods-array film on zinc plate substrate. After the modification of hydrophobic stearic acid, the film displays a remarkable superhydrophobic property with a contact angle higher than 150°. The wettability of surfaces can be adjusted and controlled by changing the content of stearic acid.

Key Words: Superhydrophobic, ZnO-Nanorods, Stearic acid, One-step route.

INTRODUCTION

Recently, superhydrophobic surfaces with the water contact angle greater than 150° have been extensively investigated due to their potential application as self-cleaning products¹. The studies have confirmed that the geometrical structure of the surface and use of low-surface energy materials play an important role in the fabrication of superhydrophobic surfaces^{2,3}. Up to now, many methods have been developed to fabricate superhydrophobic surfaces. However, most methods involve some strict conditions, high cost or complicated process and thus there is still a lack of convenient method to obtain superhydrophobic surfaces with controllable morphology. Being an important wide band-gap functional semiconductor, zinc oxide with outstanding physicochemical properties can be used in diverse range of high-technology applications⁴. It is well known that ZnO-based superhydrophobic surfaces can be fabricated *via* two main approaches: either create appropriate ZnO rough structure on hydrophobic substrates or modify the rough ZnO surface with low-surface-energy materials. According to it, herein we report a convenient one-step route and subsequent surface modification for a remarkable and controlled superhydrophobic ZnO film. Compared with other methods, the method has a simple procedure, low cost and good hydrophobic effect.

EXPERIMENTAL

Firstly, the ultrasonically treated zinc foil (20 mm × 60 mm × 0.15 mm) in absolute ethanol was placed in a sealed jar

(50 mL) containing a mixed solvent of 0.4 g NaOH and 40 mL distilled water and then left at 80 °C for 24 h. After the reaction, a bright film on zinc foil was obtained, washed with distilled water several times and dried in air at 60 °C. Then, the stearic acid were dispersed in an ethanol solution with constant sonicating for 5 min and then as-prepared ZnO films were used to immerse in ethanol suspension at 80 °C for 5 h, inducing the formation of a thin layer of water insoluble stearate on the sample surface.

The X-ray diffraction (XRD) were recorded with Philips X'Pert Pro Super diffract meter with CuK_α radiation ($\lambda = 1.54178 \text{ \AA}$). The field emission scanning electron microscopy (FESEM) was performed on JEOL JSM-6700F. The contact angles of the thin-films were measured with a contact angle meter C₂₀ (Kono, America).

RESULTS AND DISCUSSION

Fig. 1(a-c) show typical SEM images of the as-prepared ZnO films. It is found that the products are composed of highly uniform and densely packed array of nanorods, which grow almost perpendicularly onto the Zn substrates. The diameters of the nanorods range is between 150-250 nm and they have flat hexagonal crystallographic planes projecting out of the crystal seeds layer. Fig. 1d confirms the XRD pattern of the samples with the hexagonal wurtzite structured ZnO, consistent with the values in the standard card (JCPDS 36-1451).

The surface wettability of the as-prepared films has been evaluated by the water contact angle (WCA) measurement.

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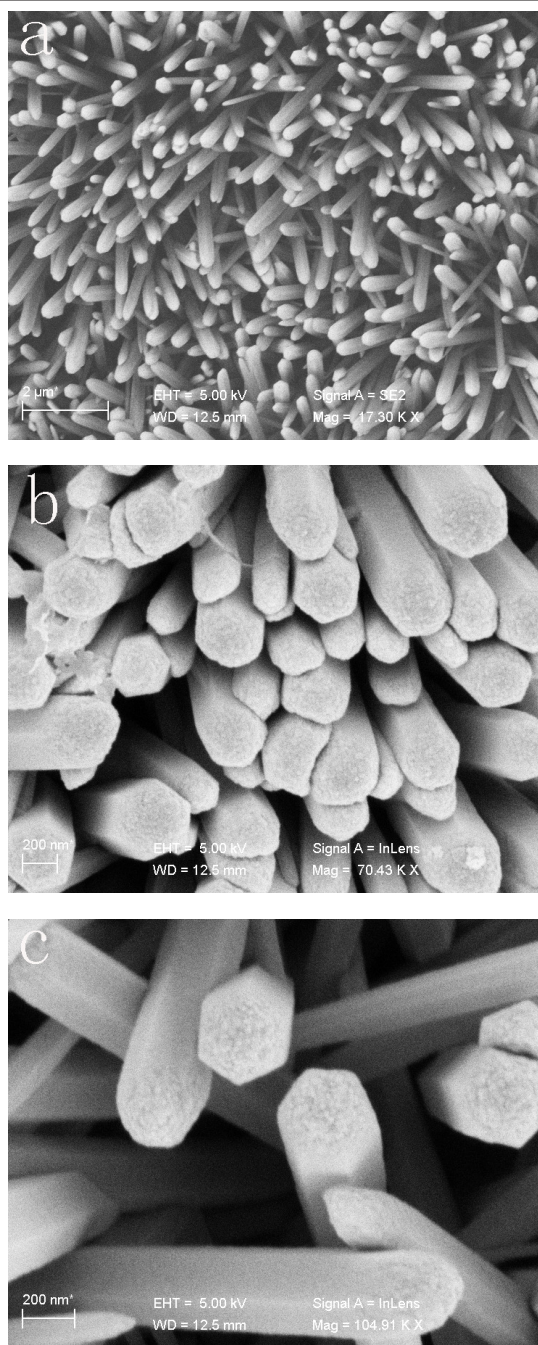


Fig. 1. (a-c) SEM images of the as-prepared ZnO film at different magnifications; (d) XRD pattern of the as-synthesized nanorod film (*:Zn substrate)

As shown in Fig. 2a, the water contact angle of pure ZnO-nanorods-array film is measured to be 48° , which is in good agreement with the hydrophilic nature of ZnO itself reported previously. Therefore, we modified ZnO nanorods by stearic acid to decrease surface energy. Fig. 2b shows that the water contact angle of the film is measured to be 157° after the dipping treatment with low-surface-energy stearic acid, exhibiting the remarkable superhydrophobicity. If the film was slightly tilted, the water droplets would roll down, indicating a very small contact hysteresis and very low adhesion.

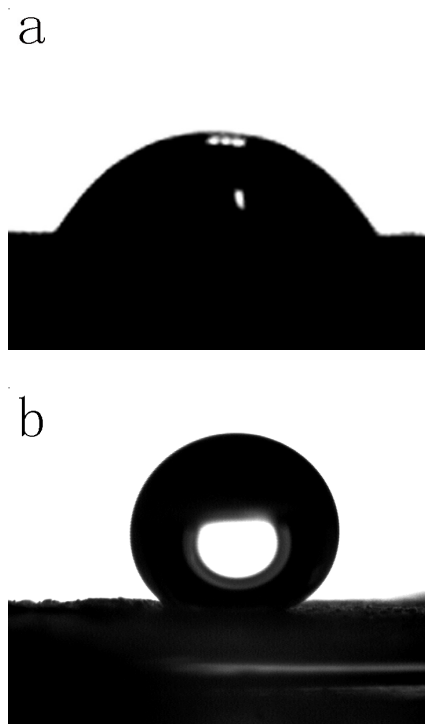


Fig. 2. Static photograph of water contact angle (a) pure ZnO-nanorods-array film without modification, (b) rough ZnO film modified with stearic acid

It is well known that the wettability of solid surface not only involves surface topography, but also relates to the modification with low-surface-energy material. In our reactive system, when the ZnO film was immersed into stearic acid solution at 80°C for 5 h, the acid groups in stearic acid could react with the ZnO seeds since there are abundant OH groups on the ZnO nanorod surfaces, forming a layer of single molecule hydrophobic film. It can decrease the surface free energy effectively, inducing the water contact angle of the surface greatly enhanced. In addition, the improved wettability of the modified surfaces relates to the content of stearic acid. As shown in Fig. 3, the corresponding water contact angles of the modified surfaces become increased constantly with the increase of stearic acid content, after 0.2 g stearic acid the water contact angle value remains almost a constant. This result means that too low a concentration of stearate did not cause enough adsorption of stearate on the ZnO surface, which can provide limited protection to the surface. Therefore, the generation of ZnO nanorod array and the modification with low-surface-energy stearic acid play a key role for this superhydrophobic surface.

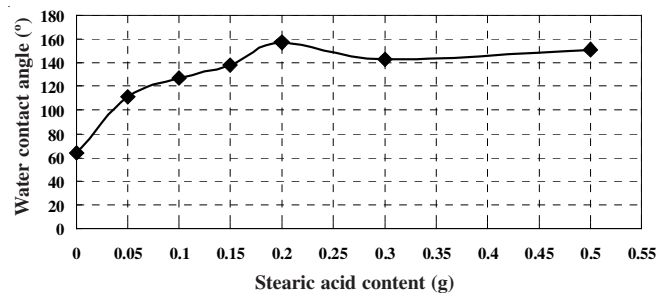


Fig. 3. Effect of stearic acid content on dipping treatment of ZnO film

Conclusion

A large scale of well-aligned ZnO-nanorods-array films on Zn substrate were successfully obtained using a simple and low-cost method. After the modification of hydrophobic stearic acid, the film displays a remarkable superhydrophobic property and low adhesion. The hydrophobicity of the thin films can be tuned and controlled by changing the content of stearic acid,

which indicates the surface treatment of ZnO nanorod array with stearic acid play an important role for improving the superhydrophobic property.

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