



Reversible surface wettability transition between superhydrophobicity and superhydrophilicity on hierarchical micro/nanostructure ZnO mesh films

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ARTICLE INFO

Article history:

Received 17 December 2012

Accepted in revised form 7 March 2013

Available online 16 March 2013

Keywords:

Superhydrophobicity

Superhydrophilicity

ZnO nanorod arrays

Water permeation

ABSTRACT

Large-area ZnO nanorod arrays were synthesized successfully on the stainless steel mesh through chemical vapor deposition route. The coated mesh shows good water permeability after ultraviolet (UV) irradiation, while it is impermeable to water after dark storage. This repeatable process suggests that the wettability transition of the rough surface is complete reversible. Besides, the special hierarchical nanostructures and the suitable size of the original mesh play an important role in smart controllability of the water permeability. The reversible transition of surface wettability has potential applications in many aspects, such as microchips, micro-fluidic devices, and biotechnology.

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1. Introduction

In recent years, the wetting/antiwetting behavior of water droplets on solid surface has become a new research focus due to its many applications, for example, in microreactors, lab-on-chip, and small droplet manipulations [1–9]. The surface free energy and geometric structure are considered to be responsible for the wettability of solid surfaces [10–14]. Many researches [15–20] have reported the preparation of various highly water-repellent surfaces, which are usually achieved by modifying hierarchical rough surfaces with low surface energy materials, or creating nanostructures on a hydrophobic surface. Recently, with the rapid development of smart surface with controlled wetting behavior, surface wettability switching between superhydrophobicity and superhydrophilicity for the photoresponsive materials such as ZnO, WO₃, and TiO₂ has received particular attention [21].

ZnO is an important oxide semiconductor with optical band gap of 3.37 eV [22]. ZnO nanostructures, especially nanowire and nanorod, are frequently employed to acquire superhydrophobic and stimuli-responsive surfaces due to their special electrical, optical, and ultraviolet (UV)-shielding properties. Many different approaches such as sputter deposition [23], hydrothermal route [7], and chemical vapor deposition route (CVD) [24] have been used to prepare kinds of ZnO nanostructure. Among these approaches, CVD route can control the crystal structure, surface morphology, and growth rate of ZnO. So it is an idea method for ZnO nanostructure growth. Liu et al. [25] have

fabricated the ZnO thin film on the sapphire substrate through CVD route, and reversible wettability switching between superhydrophilicity and superhydrophobicity is observed via alternation of UV irradiation and dark storage. The same phenomenon is observed on the sapphire substrate coated by ZnO nanorod [26]. However, most studies focus on the wettability transition between superhydrophobicity and superhydrophilicity on different solid substrate surfaces [3,8,21,27]. The corresponding research on the wettability transition and dynamic properties for photoresponsive materials on microscale pore array is lacking [22,28]. The water permeation can be well realized by regulating the pore size of the microscale pore array. As known, the water permeation process is crucial in many aspects, such as agriculture, industry, and daily life [29–32]. The most commonly used microscale pore array is stainless steel mesh due to its wide application and easy obtainment.

In this study, we present the preparation of ZnO nanorod arrays on the stainless steel mesh through the CVD route. Reversible wettability transition between superhydrophobicity and superhydrophilicity on the coated mesh is observed, and intelligent manipulation of the reversible transition can be realized via alternation between UV irradiation and dark storage. The effects of special hierarchical nanostructures and the suitable size of the original mesh on the reversible transition were studied. This work may have very important application in many fields.

2. Experimental section

2.1. Sample preparation

A stainless steel mesh (2 cm × 5 cm) with a pore size of 75 μm was used as the substrate. The mesh was cleaned with acetone for

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20 min in ultrasonic bath, and then cleaned with deionized water before being dried at 80 °C for about 10 min. Then, a 50 nm thick Au film was deposited on the mesh by ion sputtering. A quartz boat filled with Zn powders (purity 99.999%) was put in the horizontal tube furnace. The mesh was placed on the downstream side of the quartz boat and the distance between the source and the mesh was about 5 cm. Subsequently, argon was introduced into the horizontal tube furnace with a flow of 120 sccm and the pressure was kept at 120 Pa. The tube furnace was heated to 650 °C at a rate of 15 °C/min and then oxygen with a flow of 80 sccm was introduced. The reaction time lasted for 40 min. After reaction, the horizontal tube furnace was cooled down to 30 °C. The wettability of the as-prepared film was measured after it was stored in the dark for 2 weeks.

2.2. Sample characterization

The surface morphologies and the structures of samples were studied by Philips Sirion 200 scanning electron microscope (SEM) and X-ray diffraction (D/max-2200/PC, XRD), respectively. The water contact angles were measured by contact angle meter system (JY-82) with liquid droplets of 5 μ l. The surface chemical composition of the ZnO nanorod arrays was performed by X-ray photoelectron spectroscopy (Thermo ESCALAB 250, XPS).

3. Results and discussions

Fig. 1(a) shows the SEM image of the large area ZnO nanorod arrays on the stainless steel mesh. It can be seen that the ZnO nanorod arrays have a uniform arrangement on all stainless steel wire. Fig. 1(b) and (c) are the top surface SEM images of the ZnO nanorods at lower and higher magnification on a stainless steel wire, respectively. It can be seen in Fig. 1(b) and (c) that the ZnO nanorods exhibit a relatively uniform and densely packed distribution. Fig. 1(d) is the cross section image of the as-prepared ZnO nanorod arrays, it can be found that the ZnO nanorod arrays are almost perpendicular to the surface, and the heights of ZnO nanorods are about 4 μ m. Fig. 2 indicates XRD pattern of ZnO nanorods grown on the stainless steel mesh substrate. The intensity of (002) peak is much stronger than the (100) and (101) peaks. This result indicates that ZnO nanorod arrays are highly *c*-axis oriented crystallite and perpendicular to the stainless steel mesh.

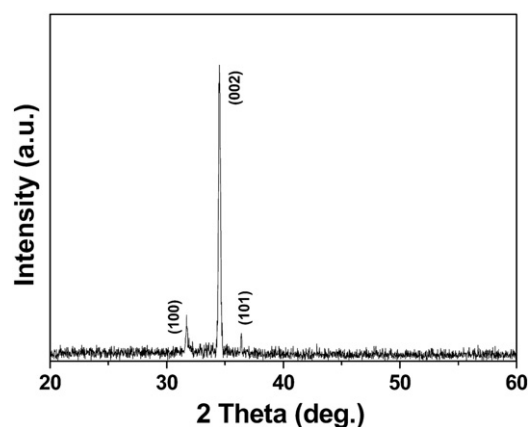


Fig. 2. XRD pattern of the as-grown ZnO nanorod arrays.

The wettability of the mesh surface which was coated by ZnO nanorod arrays was evaluated by the contact angle (CA) measurement. Fig. 3(a) depicts that the CA on this coated mesh is about $157 \pm 1^\circ$. This contact angle was measured after 2 weeks of storage in the dark. However, the coated mesh shows superhydrophilicity and the CA became 0° (Fig. 3(b)) after UV irradiation (300 W Hg lamp) for 3 h, and the water will drop down when more water is added (Fig. 3(c)). The coated mesh becomes superhydrophobic after it was put in the dark for a week. The results indicate that the water permeation process can be conveniently manipulated through the alternation between UV irradiation and dark storage. Fig. 4 shows the reversible wettability switching between superhydrophilicity and superhydrophobicity.

To acquire the information about the influence of UV irradiation on the water CA of the coated mesh, the relationship between the UV irradiation time and the water CAs of the coated mesh was studied, and the results were shown in Fig. 5. The water CAs decreased sharply from 157° to 50° at the beginning of the UV irradiation time as shown in Fig. 5. However, with the increase of UV irradiation time from 60 to 180 min, the water CAs decreased only from 50° to 0° , the wettability of the coated mesh was turned into superhydrophilicity. In order to prove that the feasibility of the coated mesh can be successfully used

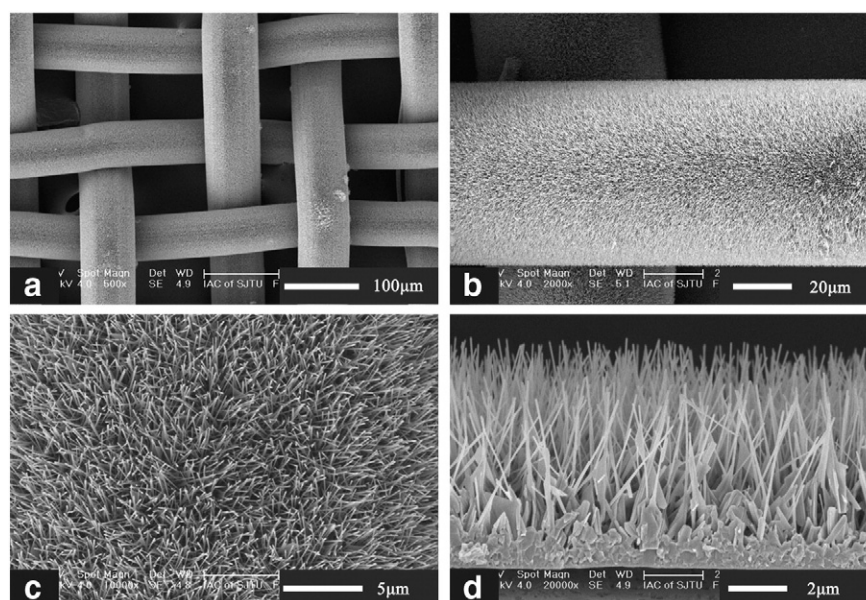


Fig. 1. SEM images of the ZnO nanorod arrays coated on the stainless steel mesh. (a) Large-area view of the coated mesh, (b) top images of the ZnO nanorods on one stainless steel wire, (c) high magnification of the as-grown ZnO nanorods, and (d) the cross section image of the ZnO nanorods with height about 4 μ m.

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