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Switchable Adhesion of Superhydrophobic ZnO Nanorod Film

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We have fabricated superhydrophobic zinc surface with reversible transformation between sliding state and adhesion by a simple hydrothermal method. Uniformly ZnO_2 nanorod was obtained at 120°C. After self-assembling of a film of n-octadecanethiol, the surface with a water contact angle (CA) of 153 ± 2°, exhibited a nonwetting property. The surface showed switchable adhesion just upon introducing UV illumination and heating treatment in turn.

Keywords: ZnO_2 nanorod, superhydrophobic, switchable adhesion, temperature

1 Introduction

Superhydrophobic surfaces with a contact angle (CA) bigger than 150°, inspired by lotus leaves, are characterized by some amazing properties, such as self-cleaning, anticorrosion, antipollution, etc. (1–3). It has drawn much attention from both fundamental research and practical applications. In practice, a material is hydrophilic when the intrinsic water CA (CA on its flat surface) is smaller than 90°, while a material is hydrophobic when the intrinsic water CA is greater than 90°, and the methods adopted to fabricate a superhydrophobic surface can be divided into two main approaches: either create a rough structure on a hydrophobic material surface, or modify the rough surface with a special low surface energy material (4–6).

Recently, considerable attention has been paid to the fabrication of intelligentized superhydrophobic surface, such as, reversible transformation between superhydrophobicity and superhydrophilicity, controllable conversion between sliding and adhesion by applying external stimuli, including light irradiation, thermal treatment, change of PH value and electric fields (7–9).

There are many reports on fabricated nano-sized structures on the surface of zincum substrate (10–13). In this report, we fabricated superhydrophobic zinc oxide with switchable adhesion by a simple hydrothermal method. The CA of the zinc oxide surface is about 153 ± 2°, and the switchable adhesion is achieved by introducing external stimulation-UV illumination and heating treatment alternatively.

2 Experiment

2.1 Preparation of Hierarchical Structure on Zincum Plate

Zincum (Zn) plates sized 10 mm × 10 mm × 0.8 mm (width × length × thickness) were used as the substrate. About 1.45 g of zinc sulfate and 3.0 g potassium hydroxide were added to 30 ml of deionized water and then stirred to form a uniform solution. Having been washed by absolute ethanol and deionized water, the Zn plates were put into the solution and maintained in Teflon-lines stainless steel autoclave of 50 ml capacity and then sealed at 100°C, 120°C and 140°C, respectively. Afterwards, it cooled to room temperature naturally. The products were collected and washed with deionized water thoroughly, and then dried in air.

The as-prepared samples were immersed in an ethanol solution of n-octadecanethiol (0.1 M) for 60 min, and finally dried the product in vacuum.

The surface chemical compositions of the as-prepared sample were analyzed by VGESCALAB210 X-ray photoelectron spectroscopy (XPS). The microstructure is determined by an X-ray diffractometer (XRD) (Philips Corp.,

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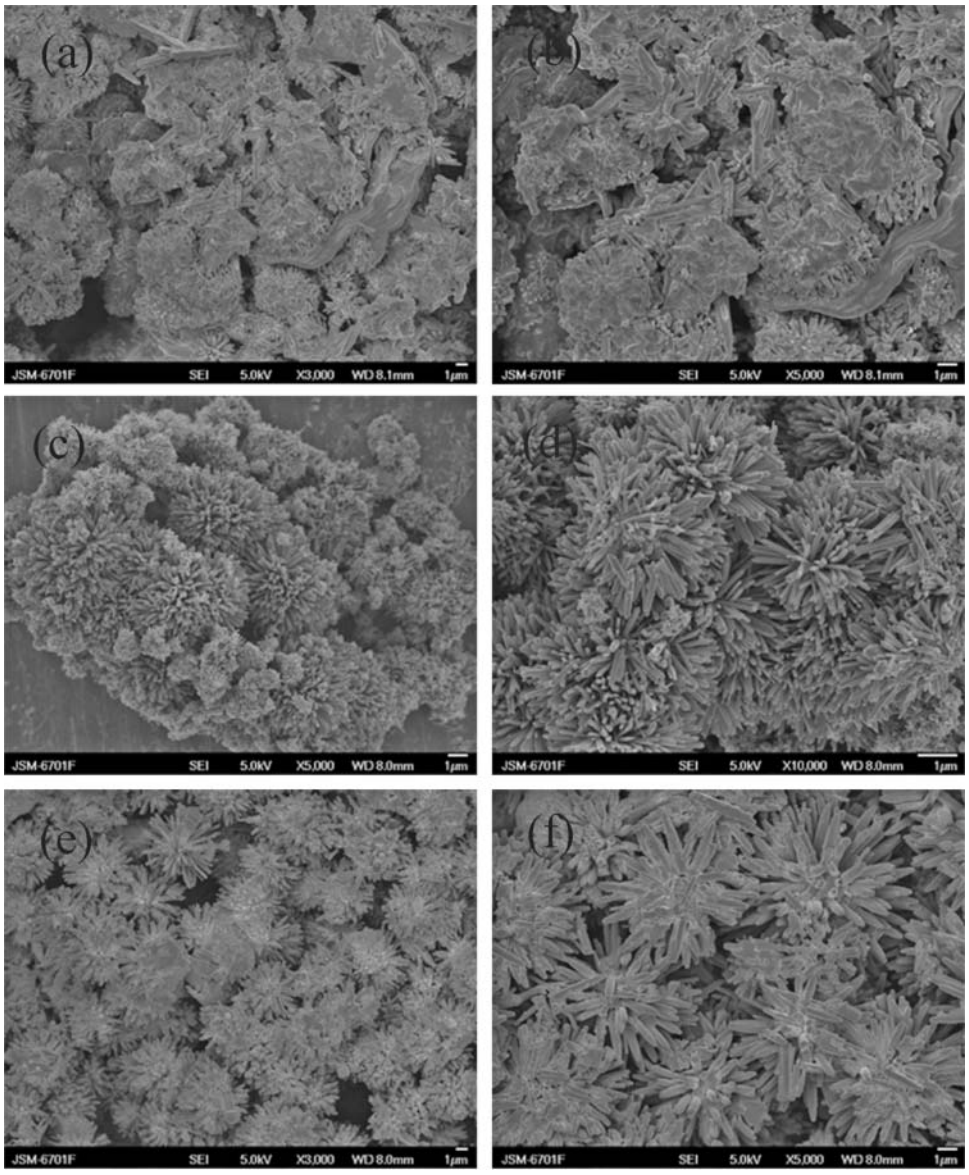

Fig. 1. Effect of the temperature on the morphological structure of Zn plate at different condition (a) at 100°C for 50 min, (c) at 120°C for 50 min, (e) at 140°C for 50 min (b, d, f) larger magnification of a, c and e.

The Netherlands) operating with Cu–Kα radiation at a continuous scanning mode and omega angle of 1.0°. The morphological structures of the as-prepared Al surface were examined by field emission scanning electron microscopy (JSM-6701F, FESEM,), and the accelerating voltage is 5–10 Kv, the vacuum pressure is 5.6×10^{-5} Pa. The sessile drop method was used for water contact angle measurements with a CA-A contact angle meter (Kyowa Scientific Company, Ltd., Japan) at ambient temperature. Water droplets (about 5 μl) were dropped carefully onto the surface. The average CA value was determined by measuring at five different positions of the same sample.

3 Results and Discussion

3.1 Effect of Temperature on the Morphological Structure

By a simple hydrothermal method, large-area nanorods cluster ZnO were *in situ* grown on the Zn substrate successfully, as illustrated in Figure 1. Uniformly, ZnO nanorods are obtained on the surface at 120°C (Fig. 1c, d). The diameter of the resulting nanorod is about 100–300 nm. When the temperature is 100°C (Fig. 1a, b), there is a little ZnO nanorod on the substrate. There are nanoparticles and short rod which are an early growth period of the rod-shaped ZnO. As the temperature increasing to 140°C

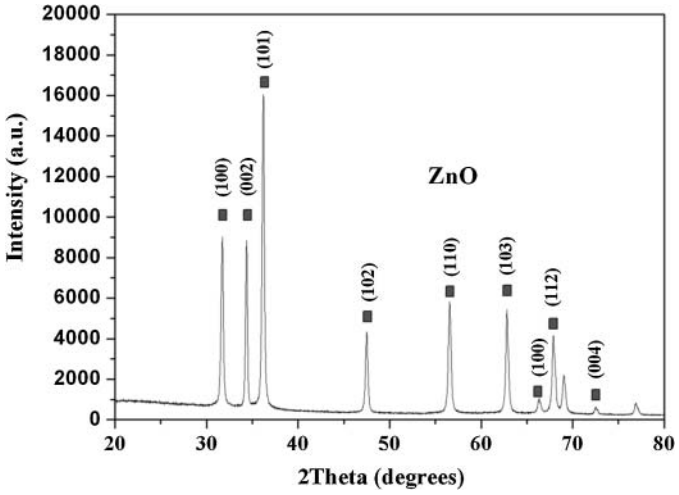

Fig. 2. XRD spectra of Zn plate maintained at 120°C for 50 min.

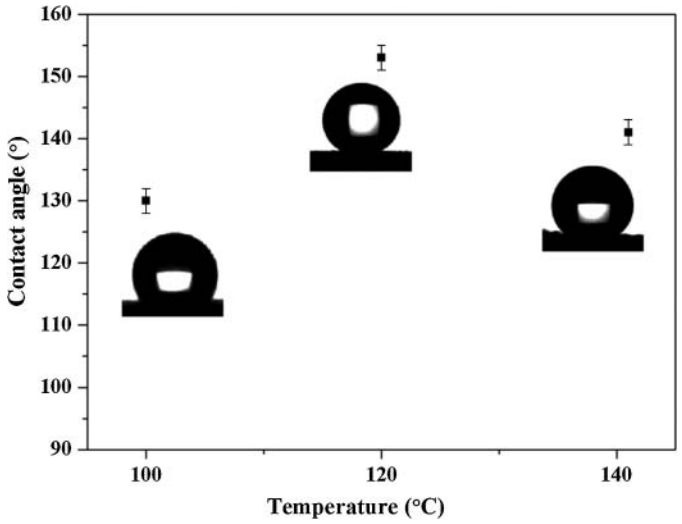

Fig. 4. Contact angle of water droplet on the prepared Zn plate maintained in an autoclave at 100°C,120°C,140°C for 50 min.

(Fig. 1e, f), the nanorods grown up with a diameter of 300–500 nm, and compared with the nanorod obtained at 120°C, the density of the nanorod of the cluster decreased.

3.2 XRD Spectra of Zn Plate Maintained at 120°C for 50 Min

Figure 2 is the XRD spectra of ZnO nanorod grown at 120°C. The diffraction peaks of 31.63°, 34.40°, 36.23°, 47.50°, 56.60°, 62.83°, 66.37°, 67.98° and 72.49° are ascribed to the(100), (002), (101), (102), (110), (103), (100), (112), and (004) crystal plane of the ZnO. And the spectra indicate that as-prepared nanorods are composed of polycrystalline zinc oxide with random crystal orientation (14, 15).

3.3 XPS Spectra of Zn Plate Maintained at 120°C for 50 Min

After immersed in an ethanol solution of n-octadecanethiol (0.1 M) for 60 mins, a film of n-octadecanethiol has physically attached on the zinc oxide nanorods. The XPS analysis was shown in Figure 3 to discuss the surface component. The peaks located in 167.7eV, 531.7eV and 1042.2 eV are attributed to the S element of the n-octadecanethiol, O element and Zn element of the ZnO (Fig. 3a). It indicated that there has self-assembling a film of thiol on the ZnO surface. Figure 3b shows The O1s peak is resolved into two components centered at 530.1 eV, 531.5 eV, which are ascribed to Zn–O–Zn and Zn–OH (16, 17).

3.4 Wetting Property of the Superhydrophobic Surface

The surface wettability of the as-prepared substrates has been studied by CA measurements. Figure 4 shows contact angle of water droplet on the prepared Zn plate, which are maintained in an autoclave at 100°C,120°C, 140°C for 50 min, respectively and modified by thiol. After having been modified by thiol, the Zn plate maintained in an autoclave at 120°C shows a contact angle (CA) of 153 ± 2° and

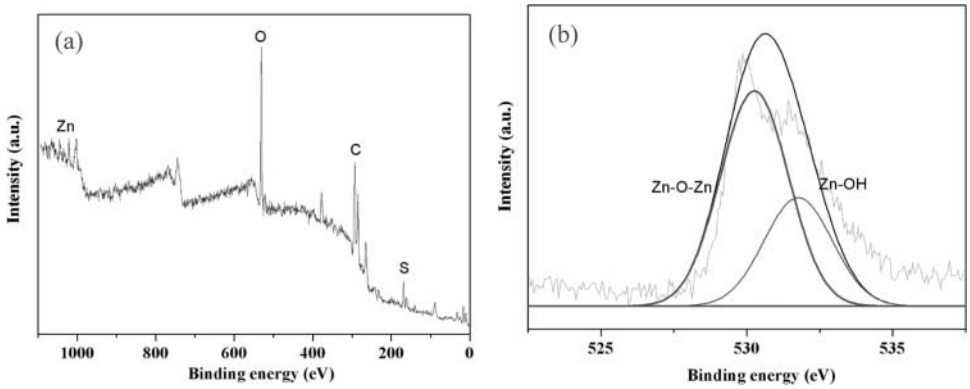

Fig. 3. XPS Spectra of Zn plate maintained at 120°C for 50 min.

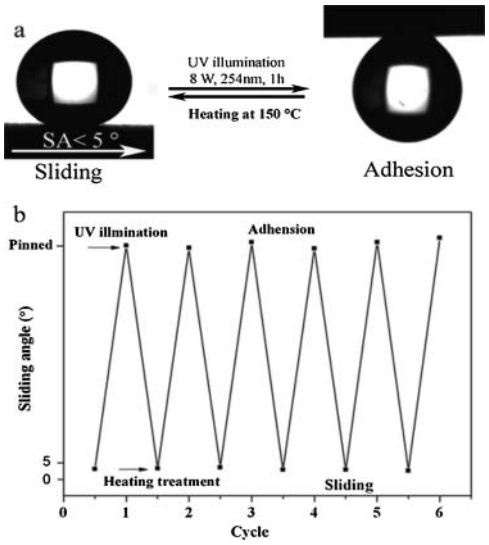

Fig. 5. (a) Photographs of a spherical water droplet with a CA of (153 ± 2°), an SA lower than 5 ± 2° (left), and a liquid drop suspended under the superhydrophobic ZnO surface before and after UV illumination, respectively, (b) Reversible adhesion transition of the surface by alternating UV irradiation and heating treatment for several cycles.

exhibited a nonwetting property. The water droplets are barely able to stick to the surface, as a sliding angle of around 5 ± 2° on the surface allows the droplets to roll off quite easily. Additionally, the CA is almost unchanged at ambient temperature for one week, which means the prepared surface has a certain extent of durability in this condition. As the surface roughness plays an important role in fabricating superhydrophobic surface, the CA of as-prepared surface varied with the change of temperature. After modified by octadecanethiol, the CA of Zn plate maintained in autoclave at 100°C and 140°C are 130° and 141°, respectively, which are induced by the decreased surface roughness.

3.5 Reversible Transformation Between Sliding State and Adhesion

The reversible switching of the ZnO plate between sliding state and adhesion was evaluated by the water contact angle measurement. Figure 5a shows a spherical water droplet with a CA of 153 ± 2°. After UV irradiating (obtained from an 8 W Hg lamp with a wavelength 254 nm) for 1 h, the water droplet is adhesive on the ZnO surface. After being heated at 150°C for 1 h, the superhydrophobicity of the coating was obtained again. This process has been repeated several times, and good switchable adhesion was observed as shown in Figure 5b.

In order to thoroughly understand the switchable adhesion of the ZnO film, the chemical composition is considered. After being modified with thiol, the ZnO surfaces are covered by oriented alkyl chains, rendering the surfaces superhydrophobic and and making the water droplet roll easily. When irradiated by UV light, the hydroxyl groups are produced (18, 19), which are hydrophilic so as to enhance the surface adhesion. To investigate the local chemical changes, XPS analysis is carried out. As shown in Table 1, by analyzing the O1s band profile, it has been found that a relative amount of oxygen in hydroxyl groups (Zn—OH) is increased after the UV irradiation. Upon heat treatment, the irradiated surface comes back to the original low adhesive state, and is attributed to the decrease of the hydroxyl groups on the surface.

Table 1. The amount change of the Zn—OH groups after different treatment

Treatment	*Zn—O—Zn/Zn—OH*
Before UV irradiation	66.48%/33.52%
After UV irradiation	43.21%/56.79%
After heating	52.14%/47.86%

4 Conclusions

In this work, we have fabricated superhydrophobic ZnO_2nanorod surface with CA of 153 ± 2° by a simple hydrothermal method. The reversible transformation between sliding state and adhesion are obtained by introducing UV illumination and heating treatment alternatively. It may have a variety of applications in industry for its anti-pollution, self-cleaning and anti-icing properties.

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