Wettability and formation mechanism of ZnO micro-spheres composed film*

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This paper reports that the film composed of flower-like ZnO micro-spheres, which consists of nano-sheets, is fabricated by chemical bath deposition. By adding hydrogen fluoride (HF) into the reaction solution, which contains zinc nitrate hexahydrate and hexamethylenetetramine, the ZnO crystal growth process is changed and the film composed by ZnO micro-spheres is obtained after keeping the reaction solution at 95 °C for 2 h. The morphology, crystal phase and wettability of the sample are characterized by scanning electron microscope, x-ray diffraction and contact angle meter, respectively. The results show that the film has the micro-nano compound structure. After modification with heptadecafluorodecyltrimethoxy-silane, the wettability of the film changed from superhydrophilicity to superhydrophobicity, on which water contact angle and the sliding angle are 154° and less than 5° for 8-μL water droplet, respectively. Additionally, the formation mechanism of the ZnO micro-sphere is also discussed.

Keywords: ZnO, micro-sphere, hydrogen fluoride, superhydrophobic, formation mechanism

PACC: 6150C, 6810C, 6820

1. Introduction

Wettability is an important property of the solid surface, which has a significant impact on our daily life as well as on industrial processes. According to the contact angle (CA) of water droplet on a solid surface, the surface can be defined as a hydrophobic (CA$>$ 90°) or hydrophilic (CA$<$ 90°) surface, extremely, a superhydrophobic (CA$>$ 150°) or superhydrophilic (CA$<$ 10°) surface. Due to their potential applications in self-cleaning,[1,2] anti-snow/fog[3] and reducing flow resistance,[4] superhydrophobic surfaces have aroused a lot of interests of researchers from both fundamental science and practical application. It is believed that the superhydrophobicity of solid surfaces depends on two factors: micro-nano compound roughness structure and low surface energy.[1,5] Currently, there are two main routes to fabricate superhydrophobic surface: building micro-nano compound roughness structure on low surface energy material,[6] and lowering the surface energy of roughness structured surface.[7] Following the second route, many kinds of ZnO-based superhydrophobic films, such as nanorods based films,[8,9] fibre based films,[10] and dandelion-like micro-sphere-based films[11] etc., have been fabricated by various methods.

Among these methods, chemical bath deposition method is a relatively simple and inexpensive one, which can be easily applied to fabricate many kinds of structured ZnO films by controlling reaction conditions, such as temperature, solution concentration, PH value and reaction time. In recent researches, some novel structured ZnO films were fabricated by adding organic compound or inorganic ion additives into the reaction solution. Tian *et al.* prepared ZnO nano-plate by adding sodium citrate into the reaction solution.[12] Yamabi *et al.* fabricated cellular films consisting of ZnO nano-sheet by the mediation of phosphate anions.[13] Boyle *et al.* reported that the growth along c axis of ZnO crystallites was promoted by the presence of acetate in the reaction solution.[14]

In this paper, we fabricated the ZnO film consisting of micro-spheres by adding HF into the reaction solution. The as-obtained film shows superhydrophilic property. However, after modified with heptadecafluorodecyltrimethoxy-silane (HTMS), the film shows a good superhydrophobic property with water CA 154° and SA less than 5°. At the same

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time, the effect of the growth time on the morphology was investigated, and the formation mechanism of the ZnO micro-sphere was discussed.

2. Experiment

2.1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), hexamethylenetetramine ($C_2H_{12}N_4$,), hydrofluoric acid (HF, 40 wt%) and toluene (C_7H_8) were all of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The HTMS was made by Dow corning corporation (USA). Glass slides were used as substrate and deionized water ($\rho = 18.25$ MΩ·cm) was used in the whole experimental process.

2.2. Sample preparation

The glass slides (1 cm×1 cm) were ultrasonically cleaned in acetone, alcohol and deionized water for 10 min, respectively, and finally dried at 80 °C in air. Additive solution HF (5 vol%) was prepared by mixing 1-mL HF (40 wt%) with 19-mL water. An equimolar (0.1 M) aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine were prepared, and 20 mL of each solution was mixed together in a plastic beaker. The mixed solution was ultrasonically treated for 5 min to make a uniform solution. Subsequently, 600-μL additive solution was added into the mixed solution and ultrasonically treated for 5 min. After putting glass slides into the beaker, the reaction solution was kept in water bath at 90 °C for 2 h. At last, the as-obtained samples were rinsed with deionized water to remove the ions possibly remaining in the films and finally dried at 80 °C in air. For investigating the effects of the growth time on the morphology of the sample, the growth time were set as 0.5 h, 1 h and 1.5 h.

For lowering the surface energy, the film was put in a sealed weighting bottle, in which there was a small vessel with 1-mL HTMS toluene solution (5 vol%). Then the weighting bottle was sealed and put in an oven kept at 80 °C for 6 h. Then, the sample was taken out and cooled in fuming cupboard.

2.3. Characterization

The morphologies of the as-prepared samples were observed by scanning electron microscope (SEM, JSM-5600LV, JEOL Ltd., Japan) operating at 20 keV. Water CA and sliding angle (SA) were measured by CAST2.0 CA analysis system (Solon (Shanghai) Information Technology Co. Ltd., China) at ambient temperature. The 8-μL water droplet was used to measure the CA and the SA. The CA measurements were repeated five times at different positions of the sample, and the mean value was reported. The SA was determined by slowly tilting the sample stage until a water droplet started to move. The crystal phase of the ZnO micro-sphere composed film was obtained by x-ray diffraction (XRD, MXPAHF, MAC Ltd., Japan) with Cu Kα radiation ($\lambda = 1.54506$ Å, 1 Å=0.1 nm).

3. Result and discussion

3.1. Morphology, crystal phase and wettability of the ZnO film

The SEM was used to observe the morphology of ZnO film. Figures 1(a) and 1(b) show the ZnO film at different magnifications.

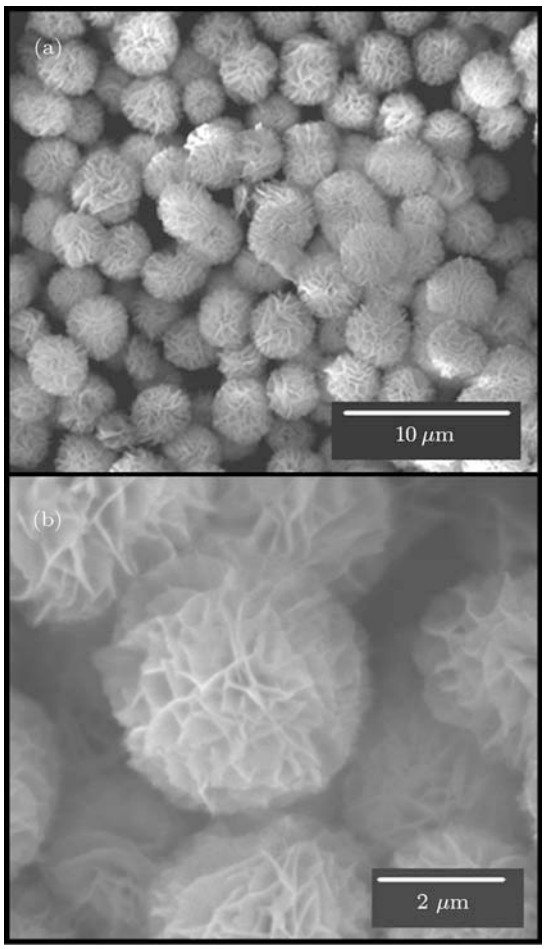


Fig. 1. The SEM pictures of ZnO micro-sphere composed film at different magnifications: (a) ×2500; (b) ×9500.

It is clear to see that dense micro-spheres were deposited on the glass slide during the given growth process. The mean diameter of micro-spheres is about 5 μm, and they are composed of nano-sheets with a mean thickness about 90 nm. The film composed by these ZnO micro-spheres has a micro-nano compound structure, which is propitious to enhance the wettability of the film from the point of the theoretical conclusion. Figure 2 shows the XRD pattern of ZnO-microspheres composed film. The diffraction peaks can be well assigned to the hexagonal-phase ZnO reported in the literature (JPCD card no. 36-1451; Wurtzite-type, space group $P6_3mc$). Compared with the standard card, the (002) peak is stronger, revealing the [001] oriented growth of ZnO nano-sheets.

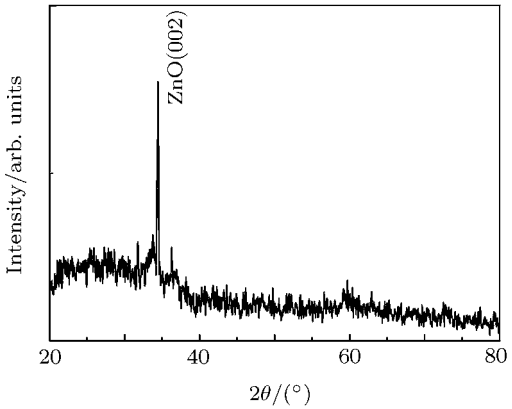


Fig. 2. The XRD pattern of ZnO micro-sphere composed film.

The wettability of the sample was characterized by CA meter. Figures 3(a), 3(b) and 3(c) show the CA of a water drop on the ZnO film (unmodified), ZnO film (modified with HTMS) and glass slide (modified with HTMS), respectively. As figure 3(a) shows, the CA of a water droplet on the unmodified film is almost 0°. In the experimental process, the droplet quickly spread out as soon as it contacted the film. This state is always called superhydrophilicity. On contrary, the water droplet could not adhere to the modified film, until the volume of the droplet increased to 8 μL. The CA (Fig. 3(b)) is 154° and the SA less than 5° for an 8-μL water droplet. The modified film is in superhydrophobic state and has self-cleaning function. As the CA of a water droplet on the modified flat glass (Fig. 3(c)) is about 114°, which is in accordance with the work of Gong *et al.*,[9] the superhydrophobicity of the modified film can be attributed to the micro-nano compound structure of film and the low surface energy of the HTMS. There are two theoretical models (Wenzel model and Cassie–Baxter model) to guide the superhydrophobic study. In Wenzel model,[15] water droplet penetrates into the rough surface, and is hardly to tumble. As described by Wenzel model,

$$\cos\theta_{\rm r} = r\cos\theta_{\rm s}, \tag{1}$$

in which $\theta_{\rm r}$ is the apparent CA on a rough surface, while $\theta_{\rm s}$ is the intrinsic CA on a flat surface, the surface roughness ($r > 1$) can enhance both the hydrophilicity and the hydrophobicity of the surfaces. Before modified with HTMS, the film shows superhydrophilic property, which is ascribed to the enhanced surface roughness by micro-spheres and the hydrophilic property of the ZnO materials. However, this is different from the reports that the ZnO is hydrophobic.[16−19] The different results may be ascribed to the hydroxyl absorption on the sample, which will make the surface energy increase.[17] It is believed that the amount of hydroxyl absorption on ZnO sample will reduce after high temperature treatment or storing the sample in dark.[17,18] The as-prepared samples were stored in air, hence more hydroxyl groups were attached on their surfaces. This difference makes the as-prepared ZnO sample showing hydrophilic property. The similar phenomenon could be found in reported works.[9,20−22]

The modified film shows a good superhydrophobic property with a high water CA (154°) and low SA (less than 5°). This phenomenon does not accord with the Wenzel model that the water droplet hardly tumbles. However, in Cassie–Baxter model, water droplet suspends on the rough surface, and is easily to tumble by proper control of the surface roughness.[23] So the wettability of the modified film can be illustrated by the Cassie–Baxter model:[24,25]

$$\cos\theta_{\rm r} = f(\cos\theta_{\rm s} + 1) - 1, \tag{2}$$

in which $\theta_{\rm r}$ is the apparent contact angle on the heterogeneous surface, while $\theta_{\rm s}$ is the contact angle on the flat surface coated with HTMS and f is the surface area fractions of ZnO component, which has been grafted with HTMS. In this experiment, $\theta_{\rm r}$ and $\theta_{\rm s}$ are 154° and 114°, respectively. The calculation result from Eq. (2) shows that f equals 0.17, which represents that about 83% of the observed contact area beneath a water droplet is air. This result implies that the water droplet suspends on the air film trapped between the micro-sphere and micro-sphere as well as between nano-sheet and nano-sheet. As a result, the water droplet minimizes its surface tension and interfacial energy by keeping sphere-like. With high CA and low SA, the film prepared in this experiment is deemed to have good properties of self-cleaning and resistance reduction.

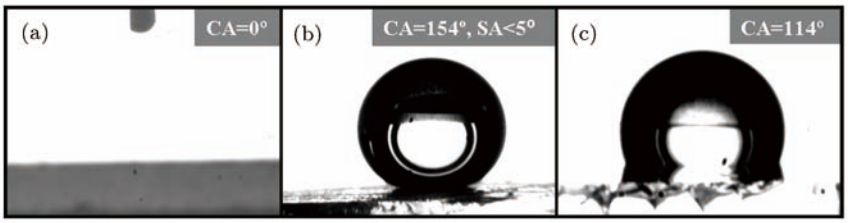


Fig. 3. The optical photo graphs of a water drop on (a) ZnO film (unmodified), (b) ZnO films (modified with HTMS), (c) glass slide (modified with HTMS).

3.2. The growth mechanism of micro-sphere

To investigate the growth mechanism of the micro-sphere, we changed the growth time from 0.5 h to 1.5 h with the interval of 0.5 h. The morphologies of the obtained samples were observed by SEM.

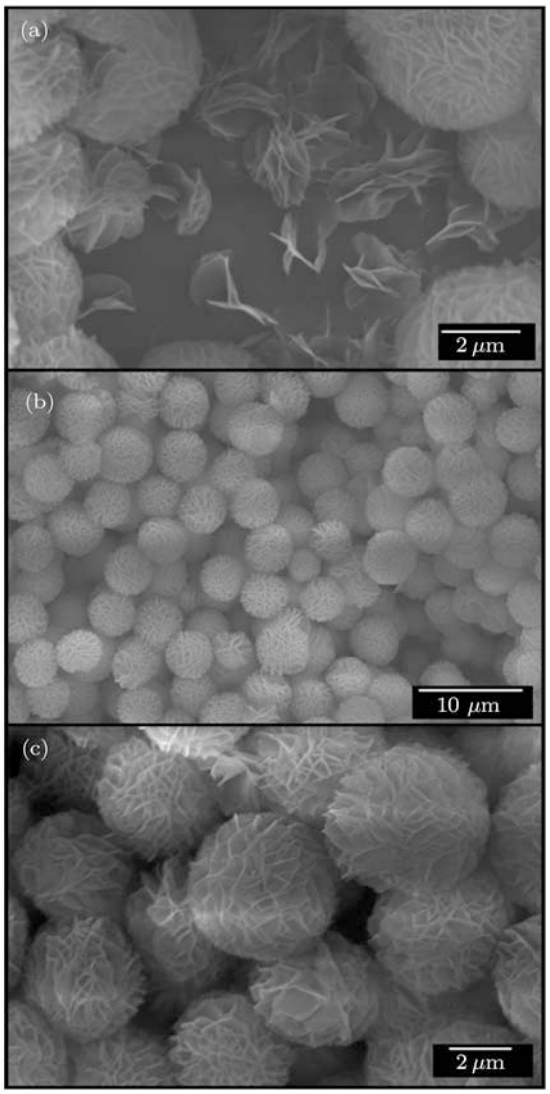


Fig. 4. The SEM pictures of ZnO films with different growth times: (a) 0.5 h; (b) 1.0 h; (c) 1.5 h.

From Fig. 4, it is implied that ZnO micro-sphere can be obtained even in 0.5 h, and the three films are all composed of ZnO micro-spheres. Compared Fig. 4 with Fig. 1(a), the morphologies of the obtained films change a little in two hours. But from Fig. 4(a), we can get a clue that may facilitate us to illustrate the forming mechanism of the micro-spheres. As shown in Fig. 4(a), some nano-sheets and half-formed micro-spheres dispersed on the bottom of the film.

The forming process of micro-spheres may accord with the illustration in the scheme (Fig. 5).

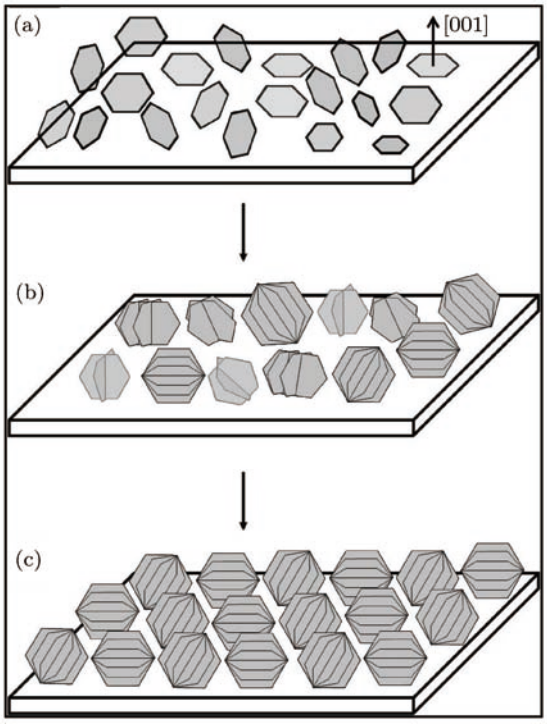


Fig. 5. Scheme of the growth process of ZnO micro-spheres.

First, ZnO nano-sheets are formed in the solution (Fig. 5(a)). As Yamabi *et al.* have calculated by computer,[13] F^- strongly coordinates with Zn^+ under the acidic condition and is absorbed on the ZnO (002) crystal plane. Then the crystal growth in the

[001] direction is suppressed and the growth units are flattened. Hence, nano-sheets prefer to grow perpendicularly to c axis. As figure 5(a) shows, some hexagonal nano-sheets are dispersing on the substrate (as shown in Fig. 4(a)). The secondary nucleation is favoured more on the ZnO nanosheets than on glass substrate because of the lower nuclei/nanosheets interfacial energy. The newly grown nano-sheets stick to the previous ones, and form the mixed nano-sheets as shown in Fig. 5(b). The mixed structures are the initial formation of the ZnO micro-spheres, and could be seen in Fig. 4(a). These mixed nano-sheets continue growing and enlarging. At last, the micro-spheres are formed. The formation process is just as the layered basic zinc acetate micro-spheres reported in the work of Hosonon, *et al.*[26] From the XRD pattern (Fig. 2), it can also be deduced that the micro-spheres are composed by nano-sheets for the strong (002) peak. The scheme illustrated in Fig. 5 well agrees with the experimental results. However, the reason why the micro-spheres are uniform (mean diameter 5 μm) is still unclear and needs to be investigated in future.

4. Conclusions

In summary, we have presented a simple method to fabricate superhydrophobic surface based on ZnO micro-spheres. The formation mechanism is attributed to the special absorption of F^- on the ZnO (002) crystal plane. Then ZnO nano-sheets were produced and mixed together to form the ZnO micro-sphere.

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