# Superhydrophobic zinc oxide film: effect of hybrid nanostructure on hydrophobicity and wetting stability

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Published in Micro & Nano Letters; Received on 13th March 2013; Accepted on 4th April 2013

Superhydrophobic surfaces have been attracting research interest in the areas of self-cleaning, drag reduction and fog condensation. However, many artificial superhydrophobic surfaces may be wetted under fluidic pressure and lose superhydrophobicity. To address this issue, the effect of surface morphologies on hydrophobicity and wetting stability should be investigated thoroughly. In this study, the authors describe a hybrid ZnO nanostructure which can be achieved by hydrothermal method. The hybrid nanostructure is constructed with a ZnO nanorods layer topped with a porous ZnO layer. The specific assembling format of the ZnO layers enhanced the stability of superhydrophobicity.

**1. Introduction:** There are two famous regimes to describesurface wettability [1, 2]. In the Wenzel state, there only exists a liquid/solid interface on the liquid base [1]. In Cassie-Baxter's theory the liquid droplet is not completely in contact with the solid surface, but forms solid/liquid and air/liquid multiple interfaces [2]. Benefitting from the steadily decreased solid fraction, the sliding angle in the Cassie-Baxter state is extremely small; therefore superhydrophobic surfaces in this state have attracted numerous research interests in the areas of self-cleaning, drag reduction of ships' shells and fog condensation [3, 4].

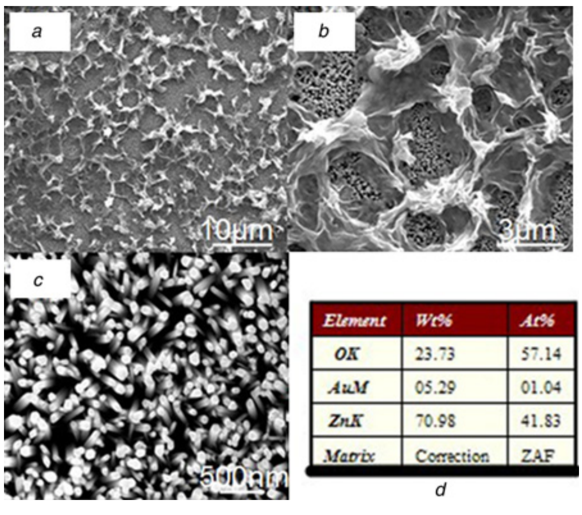
Generally, superhydrophobic surfaces can be achieved by two approaches: one is constructing nanostructures based on hydrophobic bulk materials, and the other one is applying low surface energy coatings onto the structured surfaces. Inspired by these ideas, superhydrophobic surfaces in the Cassie-Baxter state with high water contact angle (CA) and low sliding angle have been achieved on different substrates, such as metals, polymers, semiconductors and glass by different experimental approaches [5–7]. However, except from the realisation of this state, increasing interest has been paid to the mechanism study on this unique phenomenon, for example, the effect of different micro or nanostructures on surface wettablility, especially on wetting stability, which is expected to play an important role in the generation of stable water resistant surfaces or slip enhanced microfluidics platforms [8, 9].

In another case, as the great diversity of structure and multifunctional properties, ZnO nanomaterial stands out as a good candidate for this study. We present herein a hydrothermal method with designed reaction time and zinc acetate concentration to prepare a hybrid nanostructure, which is constructed with a ZnO nanorods layer topped with a porous ZnO layer. This new nanostructure provides a good opportunity to study the wetting mechanism. Benefiting from the porous layer, the fluidic pressure applied on the liquid/air interface between nanostructures is decreased steadily; therefore wetting stability is improved.

**2. Experiment:** The glass substrate (soda lime type with surface roughness below 10 nm) with a size of $10 \times 50 \times 1$ mm was ultrasonically cleaned in ethanol and deionised water in turn, then it was placed onto the temperature invariable (400°C) hotplate. A zinc acetate solution with concentration of 0.2 M was sprayed onto the glass substrate for 15 min to generate the ZnO seed layer. At the same time, the Zn-precursor was prepared by dissolving 4 mM zinc acetate into 50 ml deionised water in a vessel at 60°C and then cooled down to room temperature. Several drops of ammonia were added into the Zn-precursor to create an alkaline environment (pH value at 10), which was kept constant by sealing the vessel carefully. The glass substrate was then immersed into the Zn-precursor after being cooled down in natural atmosphere for 10 min, and then heated at 95°C for 6 h. Finally, a dehydration step was carried out in a drying oven at 100°C for half an hour just after the substrate was rinsed in deionised water for 3 min. This step was adopted to eliminate water condensation between the nanorods, which would induce a capillary force and bend the nanorods.

The surface morphology and chemical composition were observed and recorded using scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectra, respectively. A spin-coating approach (with a speed of 1500 circles per minute) was applied to deposit a uniform polytetrafluoroethene (PTFE) (DuPont USA) hydrophobic layer onto the surface. The wettability of the substrate was measured before and after the PTFE modification and confirmed by the CA measurement using a 3.0 μl water droplet. A droplet impaction experiment was also performed to justify the wetting stability of hybrid nanostructures.

**3. Results and discussion:** The SEM images of the ZnO nanostructure in different magnifications are presented in Figs. 1*a*–*c*,




| Element | Wt% | At% |
|---|---|---|
| OK | 23.73 | 57.14 |
| AuM | 05.29 | 01.04 |
| ZnK | 70.98 | 41.83 |
| Matrix | Correction | ZAF |

**Figure 1** *SEM images in different magnifications, and X-ray spectra of the hybrid ZnO nanostructure*
*a*–*c* SEM images in different magnifications
*d* X-ray spectra of the hybrid ZnO nanostructure

which clearly illustrate two different architectures. Apertures with diameters of 2–3 µm are distributed symmetrically on the cover layer, while a ZnO nanorods layer is planted at the bottom of the porous architecture.

The nanorods growth velocity in the hydrothermal experiment is controlled by fixing the reaction temperature at 95°C, while the unique nanostructure is realised by carefully controlling the reaction time and the zinc acetate concentration. During the first 3–4 h, the solution remains in a relatively stable state, that is, stable pH value, stable reaction raw materials concentration, which provides a fecund environment for effective collision between zinc atoms and oxygen atoms. As a benefit of this collision, some ZnO crystal grains are generated and floated in the reaction solution, whereas some other grains are assembled onto the substrate and results in a ZnO nanorods layer [6]. As the reaction progresses, the raw materials for the ZnO crystal growth are consuming, which makes the growth velocity of ZnO nanorods slow down and finally stop. At this point, another growth mechanism starts to play an increasingly important role in the barren solution. As the collision between zinc atoms and oxygen atoms becomes infrequent, the floated grain starts to expand in volume by combining the surrounding elements in the solution, for example, Zn positive ion and hydroxyl, which means the floated grain acts as the new growing matrix. Zinc hydroxide, for example, $Zn(OH)_2$, is therefore synthesised and deposited onto the nanorods layer. Fig. 1*d* clearly indicates the EDX spectrum of the achieved hybrid ZnO nanostructure. The effect of reaction time on the morphology is presented in Table 1. The pattern indicates that the nanostructure is mainly composed of zinc atoms and oxygen atoms. Quantitative analysis shows that the mean atomic ratio of Zn/O is around 1:1.37. This result indicates that the prepared nanostructure includes not only the ZnO crystal but also another compound composed with less zinc and more oxygen. The EDX result keeps in line with the above-mentioned mechanism explanation for the generation of hybrid nanostructures.

The wettability was determined by CA measurements using a 3.0 µl deionised water droplet. Benefiting from its high roughness factor, the unique hybrid nanostructure exhibits superhydrophilicity with a 10° water CA (see Fig. 2*a*). After being modified with PTFE, the surface wettability changed remarkably and a 165° CA is achieved (see Fig. 2*b*). Furthermore, when the water droplet was ejected against the PTFE-modified hybrid nanostructure, it rebounded back smoothly without leaving any residue on the surface. The results indicate an ideal superhydrophobicity and wetting stability under pressure on the obtained hybrid nanostructure.

According to the Wenzel equation, $\cos\theta' = r\cos\theta_0$, the superhydrophilic phenomenon is realised by a combination of high energy surface and high roughness factor. For a hydrophilic surface with an extremely high roughness factor, the right-side value of the equation can be as large as 1, which implies that the apparent CA can be 0° for an ideal condition. The ZnO nanostructure inherently possesses hydrophilicity since it is synthesised in water. Furthermore, the surface roughness factor is magnified by the hybrid nanostructure. These two factors for the superhydrophilic phenomenon are therefore satisfied on the achieved surface. On the other hand, the superhydrophobic property can be explained in terms of the Cassie-Baxter model [2]. The increased liquid/air interface fraction underneath the droplet induces a synchronously increased CA. The extreme case in the Cassie-Baxter state is that the solid/liquid and air/liquid multiple interfaces are totally replaced by the liquid/air interface, which means that the droplet is suspended on an air cushion and forms a sphere with a 180° CA. However, this is only an ideal case, as the air cushion is unstable, micro or nanostructures are therefore essential to act as the holder to maintain the liquid/air interface. The development of superhydrophobic surfaces has been extensively researched, and realisation of the surfaces with high CA is no longer a difficult problem. However, the superhydrophobicity may be ruined by fluidic gravity or motion. The unique surface morphology reported in the present work is designed to build a robust superhydrophobic surface, which is more useful in the generation of a stable water resistant or slip enhanced microfluidics platform.

The porous ZnO layer is used as the holder to support and divide the whole contact area into numerous microscale sub-units and generate the liquid/air interface with a microscale curve radius. In this case, the capillary force plays a more important role, which evidently decreases the influence of fluidics gravity and motion on wetting

Table 1 Effect of reaction time on ZnO morphology

| Reaction time | 2 h | 3 h | 4 h | 5–6 h |
|---|---|---|---|---|
| morphology | nanorods (~2 µm) | nanorods (~3 µm) | nanorods (~4 µm) | hybrid nanostructure |

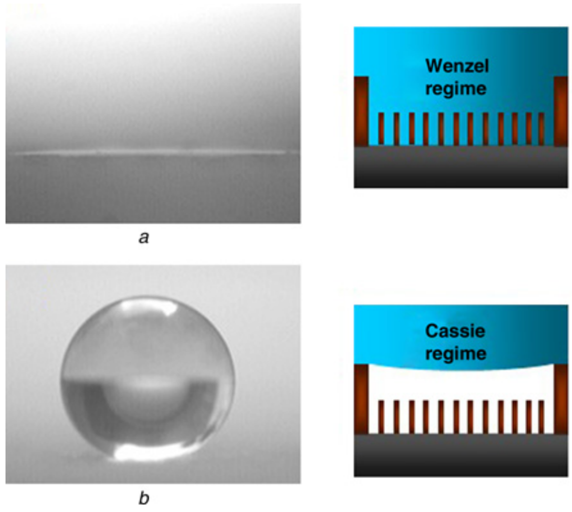



**Figure 2** *Water droplet shapes on the hybrid nanostructure*
*a* Before PTFE modification
*b* After PTFE modification, and the corresponding wetting regimes

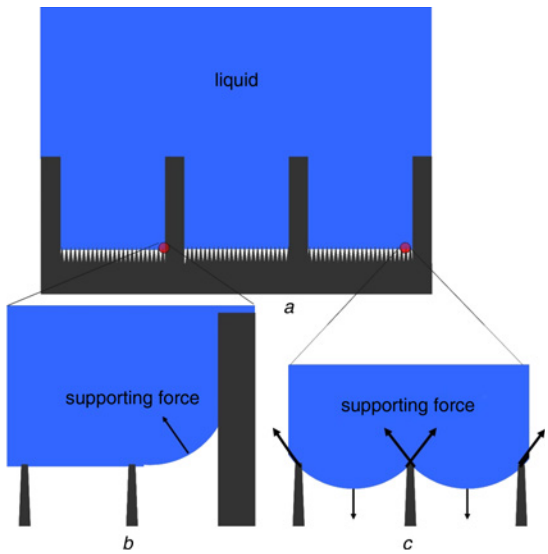



**Figure 3** *Illustration of liquid/air interface in hybrid nanostructure*
*a* Overall image
*b* Interface in the microscale structure corner
*c* Interface between nanostructures



*Micro & Nano Letters*, 2013, Vol. 8, Iss. 6, pp. 271–273
doi: 10.1049/mnl.2013.0143

stability, and holds the liquid/air interface steadily. Furthermore, the nanorods layer possessing nanoscale gaps provides an additional protection and prevents unexpected liquid invasion. The nanoscale curve radius of the liquid/air interface between the nanorods gives birth to a huge surface tension supporting force and stabilises the air cushion, which provides assistance for the generation of a stable Cassie state. The effect of this hybrid nanostructure on wetting stability is illustrated in Fig. 3, the liquid/air interface formed on this hybrid nanostructure gets duplicate protection and is therefore more stable than the one formed on the single scale nanostructure. When the fluidic pressure overcomes the supporting force on the microscale liquid/air interface, the advancing liquid/air interface would not wet the microstructures completely, but leave an air cushion in the corners (Fig. 3*b*). In this case, the capillary force is still working in the wetted microstructures, and supplying supporting force to offset the fluidic pressure. Benefiting from the porous layer, the fluidic pressure applied on the nanoscale liquid/air interface is decreased steadily (Fig. 3*c*), which stabilised the Cassie-Baxter state. This assembling format will be interesting for fabrication of robust superhydrophobic surfaces.

**4. Conclusion:** A hybrid ZnO nanostructure constructed with a unique porous cover layer and ZnO nanorods bottom layer was prepared by a simple hydrothermal method on a glass substrate. The experimental results proved that the reaction time and the zinc acetate concentration have played an important role in the generation of this hybrid nanostructure. The porous ZnO layer and the ZnO nanorods layer have enhanced the surface roughness and provided duplicate protection from liquid/air interface invasion, which contributed to a stable superhydrophobic surface. Concerning the stable water resistant property and the special optical property of ZnO materials, such a nanostructure may have potential applications in optoelectronic coupled microfluidics devices.

**5. Acknowledgments:** This research was supported by the National Basic Research Programme of China (grant numbers 2013CB328803 and 2010CB327705), and the National High Technology Research and Development Programme of China (grant numbers 2012AA03A302 and 2013AA011004).

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