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## ENHANCED ADHESION OF SUPERHYDROPHOBIC ZnO SURFACE

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### ABSTRACT

The superhydrophobicity and the strong solid-liquid adhesion of the dually structured ZnO surface are attributed to the suitable size of microstructure and nanostructure. This phenomenon, so different from the *Lotus effect*, can be called the *Petal effect*— the super hydrophobicity and the enhanced solid-liquid adhesion coexist on the same surface. The Cassie impregnating model was proposed to understand the underlying reason.

**Keywords:** hydrophilicity, hydrophobicity, wettability, Van der Waals force, adhesion

### INTRODUCTION

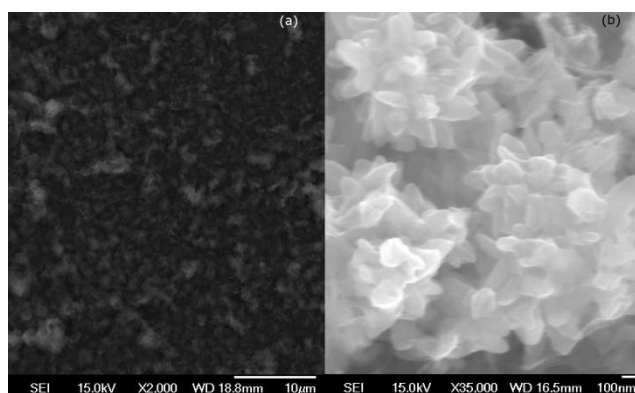
Wettability of a solid surface is a characteristic of materials governed by the surface chemical composition and the surface morphology. Finely tuning the wettability of a solid surface has proven very challenging in surface engineering. It is believed that both hydrophobicity and hydrophilicity can be amplified by the roughness of a solid surface, so there have been lots of artificially roughened substrates which are experimentally constructed to be strongly hydrophilic or hydrophobic (Bico et al. 1999). As far as the strong hydrophobicity or superhydrophobicity (generally the contact angle is larger than  $150^\circ$ ) is concerned, the dual scale (microscaled and nanosized) roughness appears to be essential (Nosonovsky and Bhushan 2007; Wang et al. 2007) since the lotus leaf, the rose petal, the eye of pipiens (Sun et al. 2005), the leg of pond skater (Larmour et al. 2007) and so on, have a hierarchical structure which confers the superhydrophobicity (Gao and McCarthy 2006). Therefore, there have been tremendous efforts to produce those bio-inspired superhydrophobic surfaces (Cheng et al. 2005; Feng et al. 2009). However, to date, the mystery about how roughness induces non-wetting behaviors is still not unveiled. In particular, it is not clear why the lotus leaf and rose petal, which have multiscale (or hierarchical) roughness structures, both exhibit superhydrophobic property, meantime they behave so differently to the water droplets— when the water droplets fall on the lotus leaf, they effortlessly roll off with contaminants enabling self-cleaning; yet water droplets tend to be stuck on the rose petal surface even when the surface is turned upside down (Feng et al. 2008; Liu et al. 2010).

In this study, we looked into the wettability of dual scales textured zinc oxide (ZnO) surface, which are the clusters, made of ZnO, and each cluster consists of the packed ZnO nanorods. The roughness from cluster to cluster is microscaled, while within one cluster the roughness from rod to rod is down to nanoscale. It was found that mixing two scales increases the hydrophobicity, and such a structured surface imparts remarkably high adhesive force, like the controllable adhesion on the surface of titanium oxide (Lai et al. 2008), which is akin to the superhydrophobicity of rose petal.

## EXPERIMENTAL

The ZnO structured surface was prepared as follows: the solution of Zn-AD ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 0.2 M) was airbrushed onto the precleaned micro slide which was heated at 160 °C by a heating plate, in which  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was decomposed into zinc oxide seeds on the substrate. Then the seed-coated slide was put into the beaker containing the same solution but with the different concentration (0.1 M), and the beaker was in a water bath (90 °C) for 3 h. The slide was gently taken out. Before the slide was air dried, it was thoroughly rinsed by ethanol for 15 s to get rid of those residues.

Scanning electron microscopy (SEM) images of the ZnO structured surface were scrutinized by a field emission scanning electron microscope (JEOL 7401F) at beam voltage of 10 kV. The Bruker D8 Discovery diffraction system analyzed the X-ray powder diffraction (XRD) profile of the final product.



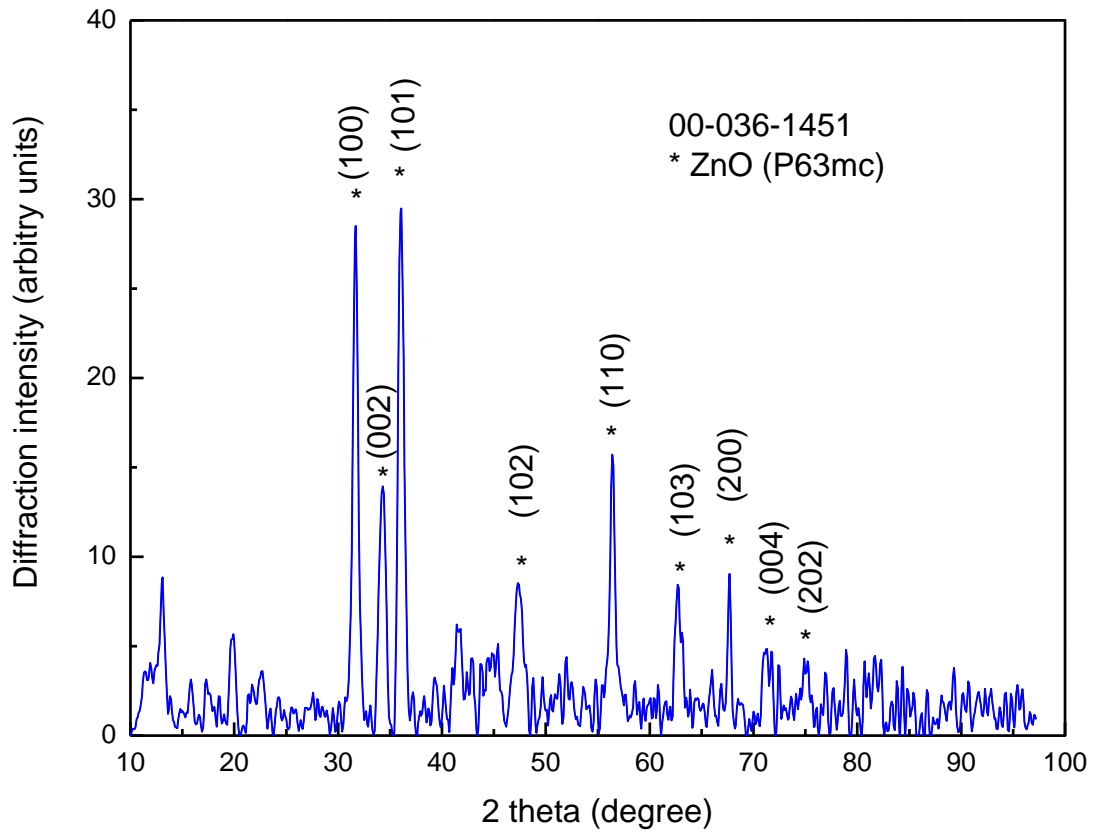
**Figure 1.** (a) SEM morphology for a large scale ZnO structured film, and (b) nanoprotrusions in the zoom-in image for ZnO surface.

## RESULTS AND DISCUSSION

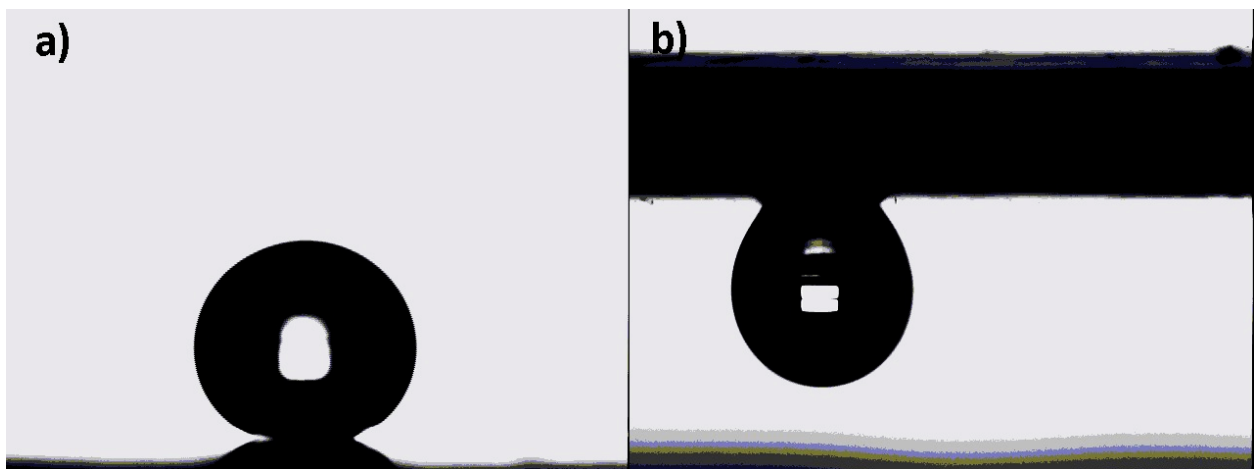
The morphology of the ZnO coated sample was checked with SEM. As shown in Figure 1, a two-scale roughness structure is clearly displayed: the micro-sized clusters and the nanosized rods. Many clusters can be found on the surface with diameters ranging from 0.3 to 0.5  $\mu\text{m}$  as presented in Figure 1(a). Figure 1(b) demonstrates that each of the clusters is composed of ZnO nanorods with about 3-4 nm in diameter. The SEM images depict that the hierarchical structures are assembled by the micro-sized clusters and the nanoscaled nanorods.

The chemical composition and crystal structure were portrayed by XRD analysis in Figure 2. The sample is single-phased ZnO in Wurzite structure with space group of P63mc. The estimated lattice constants are  $a = 3.25 \text{ \AA}$ ,  $c = 5.21 \text{ \AA}$ .

Water contact angle measurements characterize the wettability of the surfaces. Figure 3(a) presents that the water contact angle is about  $155^\circ \pm 2^\circ$ . To more carefully study the wetting behaviors, we turned the slide upside down. The contact angle  $152^\circ \pm 2^\circ$  was shown in Figure 3(b), which exhibits the surface has the very high normal adhesion (the force direction is perpendicular to the surface). In both cases, the contact angles are larger than  $150^\circ$  indicating the superhydrophobicity. When being placed inverted, the water drop still maintains its sphere shape although there is a slight



**Figure 2.** XRD characterization for ZnO structure and composition.



**Figure 3.** Wettability analysis of the ZnO surface with dual structure: (a) the surface is upright; (b) the surface is upside down.

difference, which can be understood as experimental error. Evidently the large adhesive force keeps a water droplet stuck with the surface even when being overturned. It is so different from the *Lotus effect* – the water droplet would slide off even when the surface is slightly tilted.

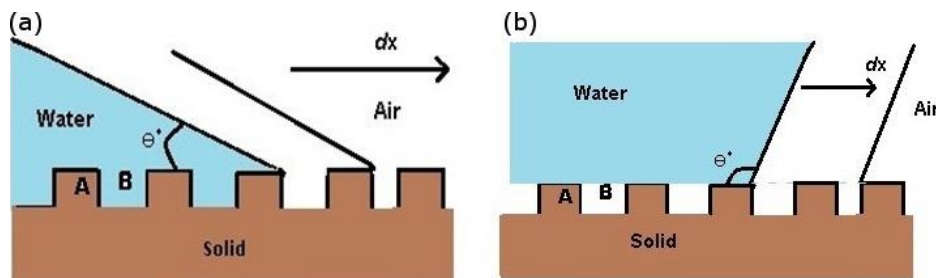
“Wenzel” (Wenzel 1936) and “Cassie-Baxter” (Cassie and Baxter 1944) are mostly adopted models for hydrophobic surfaces with one level roughness. The underlying physics for both models is the minimization of the surface free energy: the minimal of the total surface energy stabilizes the droplets of water on surfaces. Here the total surface energy includes the interfacial energies of the solid-air, solid-liquid, and water-air. Thus, an equilibrium effective contact angle  $\theta^*$  on roughened surfaces can be calculated by minimizing the free energy. Before reaching the equilibrium, a small displacement  $dx$  of the contact line, as sketched in Figure 4(a), leads to a change in surface energy:

$$dE = r(\gamma_{sl} - \gamma_{sv})dx + \gamma \cos\theta dx \dots \dots \dots (1)$$

$E$  is minimal at equilibrium. In which  $r$  stands for roughness, when  $r = 1$  (flat solid), Young’s equation is deduced:  $\cos\theta = (\gamma_{sl} - \gamma_{sv})/\gamma$ , where  $\gamma_{sl}$ ,  $\gamma_{sv}$  and  $\gamma$  denotes the interface energy between solid and liquid, solid and vapor, liquid and vapor, respectively. For a patterned surface, Wenzel’s relation is derived:

$$\cos\theta^* = r \cos\theta \dots \dots \dots (2)$$

where  $\theta$  is Young’s angle. Equation(2) predicts the following: since  $r > 1$ , roughness could amplifies both hydrophobicity and hydrophilicity (Han et al. 2004; Nakajima et al. 2000). If  $\theta > \pi/2$ ,  $\theta^*$  becomes even larger. If  $\theta < \pi/2$ , the actual contact angle  $\theta^*$  becomes smaller. According to the Equation (2) Wenzel’s interpretation, both cases can be explained that due to its roughness, the increased effective surface area reinforces both hydrophobicity and hydrophilicity: the hydrophilic situation favors the more solid/liquid contact so that water droplet tends to spread all over on a rough substrate. On the contrary, a rough hydrophobic material appears more hydrophobic because a liquid drop would be energetically unfavorable to develop a larger contact with a solid if maintaining the same contact angle.



**Figure 4.** Two wetting models: (a) the Wenzel model and (b) the Cassie-Baxter model.

When the structure on a surface becomes more protruding, the water droplets touch down its asperities by bridging the adjacent protrusions. As a result, air is entrapped so that a droplet lands on a heterogeneous surface consisting of a solid and air as illuminated in Figure 4(b).

A net change in surface free energy equals to the difference in interfacial surface tension between a dry and a wet surface,  $\gamma_{sl} - \gamma_{sv}$ , multiplied by the change in area covered by the droplet  $dx$ , as seen in Figure 4(b),

$$dE = f_A(\gamma_{sl} - \gamma_{sv})_A dx_A + f_B(\gamma_{sl} - \gamma_{sv})_B dx_B + \gamma dx \cos\theta^* \dots\dots\dots (3)$$

in which  $f_A, f_B$  represent the fractional area for  $A$  and  $B$ , respectively. At equilibrium ( $dE = 0$ ), the effective contact angle obeys the following relation:

$$\cos\theta^* = f_A \cos\theta_A + f_B \cos\theta_B \dots\dots\dots (4)$$

where  $\theta_A$  and  $\theta_B$  are the Young contact angle on domains of  $A$  (protruding islands) and  $B$ (air), respectively. According to the mathematical analysis, the contact angle on air  $\theta_B = 180^\circ$  and  $\cos\theta_B = \cos(180^\circ) = -1$ , the existence of air pockets between protrusions is instrumental in superhydrophobicity. Therefore, the more air entrapment on the roughened surfaces, the larger the contact angle would be.

Apparently, the entrapped air promotes the surfaces to be super hydrophobic. Then the equation (4) becomes: ( $1-f_A = f_B$ ),

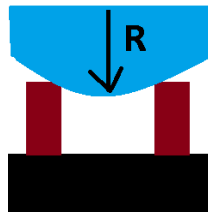
$$\cos\theta^* = f_A \cos\theta_A - (1 - f_A) \dots\dots\dots (5)$$

Equation (5) is the well-established Cassie-Baxter equation, which describes a fascinating phenomenon: the surface achieves superhydrophobicity meanwhile obtaining phenomenal slippery property because of the low hysteresis (the difference between the advancing and receding angles). In other words, the Cassie surfaces are very water repellent.

The Wenzel or Cassie-Baxter is modified to explain the wettability if there are more than one level roughness on a single surface. Only two possible extreme cases will be discussed here. The smaller scale roughness could be completely wetted, leading to the combining Wenzel on Cassie-Baxter hydrophobicity. The other one is that the smaller-level structure could be bridged, inducing the case with Cassie-Baxter on Cassie-Baxter hydrophobicity.

The water wets the smaller scaled structure (Wenzel model) but the air remains inside of the larger texture, causing a heterogeneous surface composed of air and solid, exactly as how the dual scaled roughness ZnO surface behaves which is more like the rose petal. More specifically, due to the super-hydrophobicity of the dually structured ZnO surfaces, the water droplets maintain their spherical shape, but do not roll off because the surface has a strong normal adhesion. This is commonly referred to as the petal effect in which Van der Waals interaction dominates which could force an intimate contact between the solid and the liquid, and favors a Wenzel scenario at a small scale (nanometers). With the air pocket trapped at a larger scale (micrometers), petal surfaces could ensure a very high degree of hydrophobicity. This is known as the Cassie impregnating wetting regime. It is the widely known fact that the micro- and nano-structures of rose petal are larger in scale than those structures on the lotus leaf (Feng et al. 2009). In the case of the lotus leaf, when the size of the nano-structure is so small that Van de Waals force can be negligible, the surface tension dominates based upon the Laplace equation (Quéré 2005),  $\Delta p = \frac{2\gamma}{R}$ , which illustrates the pressure difference

between the liquid and air ( $\gamma$  represents the interfacial energy between liquid and air,  $R$  is the water curvature) as shown in Figure 5.



**Figure 5.** Diagram for a water droplet sitting on the nanoprotusions (in an exaggerated manner).

The decreased spacing between nanoprotusions results in the smaller  $R$ , which would lead to the larger  $\Delta p$ , namely the larger pressure inside the water droplet. While the larger pressure in water droplet will not allow the nanoprotusions on the lotus leaf to penetrate it so that the water merely sits on the top of protruding structures. This explains that even when the lotus leaf is slightly tilted, the water droplets could not steadily stay on the surface due to the lacking of pinning of triple-phase solid/liquid/vapor contact line. Therefore, the lotus leaves fall into the Cassie-Baxter on Cassie-Baxter model. Although the surface of lotus leaf is superhydrophobic, there is not any adhesion to make the water cling to it, which facilitates the self-cleaning. Therefore, the difference between Cassie-Cassie and Wenzel on Cassie is the enhanced adhesive property of the surface — it is the reason that the water droplet would not fall off the petal or ZnO surface when the surface is tilted at any angle or turned upside down in which the nanoscaled structure modulates the adhesive property.

It was also claimed that two states, Wenzel and Cassie-Baxter, can coexist on a structured hydrophobic substrate (Lafuma and Quéré 2003). They observed that the induced direct transition between two states occurs when the pressure is exerted on the water droplet. With increasing pressure, the structured surface gradually loses its anti-adhesive property, transiting from Cassie to Wenzel state. Once the Wenzel state is realized, the surface confers the high adhesive force at the cost of loss of the hydrophobicity to some degree. For the appropriately sized two-level roughness surface (petal-like), the nanoscale structure primarily regulates the adhesive property of the surface. It was proposed that when the scale of roughness is smaller than 100 nm, Van der Waals forces could force a contact between the solid and the liquid, which makes a Wenzel scenario at this scale (Quéré 2002). Meanwhile the micro-scaled structure allows the pinning of the contact line, thus the entrapment of air and ensures the superhydrophobicity. The systematic theoretical work remains to be fully done. It would be extremely helpful if we could quantify how the wetting behaviors vary as the size of micro/nano textures changes in order to optimize the structures according to various applications.

## CONCLUSIONS

The roughness of the structured surface—consisting of ZnO clusters which are made of ZnO nanorods, suffices for superhydrophobicity and yields an enhanced adhesion to water. The surface has both properties which are ascribed to the suitable

size of micro- and nano-structures on the same surface. Like rose petals, the hierarchical structured ZnO surface renders the superhydrophobicity and being sticky to the water droplet. The tailored ZnO structures could pave the way for finely tuning the surface properties especially for the surfaces which could possess both the superhydrophobicity and the high adhesive properties. Not only does this study improve our understanding about the wetting properties of the experimentally structured even natural surfaces, but it also provides insightful guidance for the design of new patterned surfaces with desired wettability.

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