One-step to synthesize multilevel structured ZnO films with exceptional wettability

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Abstract
A facile one-step synthesis approach was developed to prepare ZnO films with multilevel structures composed of microclusters and nanohairs. The hierarchically structured ZnO films demonstrate peculiar wettability—superhydrophobicity but with high normal adhesion. The very high aspect-ratio of ZnO nanohairs minimizes the area of the (002) high potential surface which is the preferential growth direction. Microclusters of ZnO ensure the sufficient short-distance interactions for the normal adhesion, while the overall ZnO platforms with unique geometrical configuration and chemical composition provide the bulk scale conformity necessary for superhydrophobicity and high adhesion for rough or contoured surfaces. The superhydrophobicity of the ZnO nanohair films can be explained with the Cassie impregnating model or partial wetting model. Thanks to its purity as an inorganic material, the superhydrophobic ZnO films exhibit outstanding durability.

Introduction
The wetting properties of superhydrophobic surfaces have fascinated worldwide researchers due largely to their extensive applications such as anti-wetting, anti-snow (or ice), anti-dust, and reduced friction resistance by reducing solid-liquid interaction. Generally speaking, the superhydrophobic surfaces exhibit a water contact angle (CA) larger than 150°, which are typically categorized into two groups: surfaces being low adhesive to water and being high adhesive to water. In nature, lotus leaves belong to the first group. Due to low adhesion, water droplets could spontaneously roll off the lotus leaves and remove dusty particles, realizing commonly so-called ‘self-cleaning’. The surfaces on Gecko’s toes fall into the second group [1, 2]. On these surfaces, a water droplet demonstrates a static CA larger than 150°, however, it can be pinned onto the surfaces at any tilted angles [3] because of the high adhesion.

Nature knows best. In order to mimic nature to achieve super-hydrophobicity, numerous approaches, including laser treatment [4], chemical vapor deposition [5], chemical etching or depositions [6, 7], have been reported either amplifying the roughness on hydrophobic surfaces [8, 9] or modifying coating materials on a surface level to lower free energy [10, 11]. In spite of that all the involved methods are either costly complicated, or energy-intensive, in the past decades a large number of superhydrophobic surfaces have been successfully prepared such as the superhydrophobic films synthesized on copper, gold, and silver [12–14], aligned polymer nanofiber [15], carbon nanotube arrays [16] and so on.

Metal oxides are promising materials in many areas including catalysis [17–19], photocatalysts [20, 21], photovoltaic [22, 23], and optical devices [24]. Zinc oxide (ZnO) films have garnered tremendous attention since, as a wide band-gap semiconductor material, ZnO finds widespread applications in electronic devices, for example, ultraviolet laser diodes [25], photo-catalysts, gas sensors [26], light-emitting diodes (LEDs) [27] and solar cells [28, 29], owing to its phenomenal opt-electric, photocatalytic and transparent properties. ZnO nanoparticles are also utilized for antibacterial [30, 31], food industries [32], and multifunctional coatings [33, 34]. As an important property of ZnO films, up to now the wettability has not been as intensively investigated as the above mentioned other properties. On the other hand, although various strategies and
techniques can be adopted to prepare ZnO films like thermal evaporation [35], vapor-phase transport technique, powder scattering technology [36], electrospinning technique [37], atomic layer deposition [38], sol-gel [39], and self-assembly growth method [40, 41], none of them is cost-effective and environmentally friendly. In this report, we developed a facile single-step synthesis technique to prepare multi-level structured ZnO films with exceptional wettability.

**Experimental details**

A one-step facile approach was developed to synthesize multilevel structured ZnO films. A micro-slide was thoroughly ultrasonic-cleaned first in acetone and then in ethanol for 10 mins, respectively. About 1.0 grams of precursor zinc acetatedihydrate (Zn (CH$_3$COO)$_2$•2H$_2$O, 99% pure) was put into a pre-cleaned alumina crucible. The properly cleaned micro-slide acted as a lid for the crucible, placed on the top of it. Subsequently, the crucible along with the slide was put into an oven. With a ramping rate of 5 °C min$^{-1}$, the oven was heated to 300 °C and then retained at 300 °C for a time period of 6 h. Next, the entire system was naturally cooled to room temperature. Certainly, a batch of slides with ZnO film coating can be produced at one time for mass production and cost-effectiveness. The as-produced ZnO film on the micro-slide was carried out with various characterizations. The morphology images were examined by a JEOL scanning electron microscope (SEM) (JEOL JSM-7000F). Some ZnO powder was scraped off the slide for XRD study. The x-ray diffraction (XRD) pattern was collected on a Rigaku Ultima IV diffractometer in Bragg-Brentano geometry. After filtering with a K-beta filter (a 20-micron Ni foil), the copper K-alpha line ($\lambda_{Kα} = 1.54059$ Å) was utilized as a monochromatic light source. The wettability was scrutinized by an optical tensiometer. To measure the water contact angles of the ZnO films, 5 ul of deionized water droplets were dropped on the film and the water contact images are recorded and analyzed on a VCA Optima system with an accuracy of 0.5°.

**Results and discussions**

**Scanning electron microscopy**

The morphology of the ZnO films was examined as shown in figure 1 SEM images. Such a system can be regarded as a multi-level roughness structure composed of micro-sized clusters, and thin long individual hairs in each cluster, as displayed in figure 1 with different scanning scales. Apparently, the high quality and high purity micro-clusters and nano-hairs are uniformly distributed on the slide. Figures 1(a)–(d) reveal that the size of clusters ranges from 5 to 15 micrometers. As portrayed in figures 1(e) and (f), individual crystal hairs are in nanoscale with about 100–150 nanometers in diameters. The multiple scaled structures were substantiated with various scanning scales. Roughness with multiple-level features assembled on the surface with abundant entrapped air pockets among micro- and nanostructures, ensures superhydrophobicity because water droplets can rest partially on solid surface features and partially on air pockets. The appropriate chemical composition coupled with hierarchical-structure renders quite a large contact angle on the sample because the wettability of surfaces is governed by the surface morphology and surface chemical composition [42].

**X-ray diffraction profile**

The XRD profile in figure 2 corroborates further that the multi-level structured system is single phased ZnO, possessing the Wurtzite crystal structure (PDF# 36-1451) with a space group of $P63mc$ and cell constants of $a = 3.25$ Å, $c = 5.21$ Å. As disclosed in figure 2, the relative intensity of (002) reflection is much stronger than that of other peaks, say, (100) and (110), (randomly oriented powder scraped from the slide for characterization), suggesting the preferred orientation is along c-axial of the nanohairs. The intensity of (002) reflection is 58.6% higher than that of randomly oriented ZnO microcrystals that uniformly represent all crystal orientations if a large enough sample is present. This strongly suggests a preferential growth of the hexagonal ZnO nanostructures in the (002) direction and the highly oriented c-axis alignment of the nanohairs perpendicular to the substrate, as the XRD data were collected in the Bragg-Brentano geometry (2theta/omega scan). Based on the Scherrer equation, the thicknesses in [002], [100], and [110] directions are estimated to be 83, 22, and 19 nm, respectively. It also reveals the high aspect ratio (length-to-diameter ratio) of the ZnO nanohairs.

Peculiarly, the wettability of ZnO films can be attributed to their several properties. The Wurtzite ZnO structure is non-centrosymmetric which contributes to a different facets polarity [43]. The facets of (001) and (00$ar{1}$) planes are believed as polar surfaces. Therefore, the polar facets are characterized by high surface energy, resulting in the spreading out of water liquid. While the facets of (1$ar{1}$0) and (330) planes are considered as non-polar surfaces, possessing low surface energy favoring the liquid drop retraction. Additionally, a thermal treatment could make them more hydrophobic but the hydroxyl groups of non-polar facets termination lead to hydrophilic behavior in the initial state [44]. However, due to the preferential growth of ZnO along the c-axis
and a very high aspect ratio (> 100), the non-polar facets are more dominant. Therefore, ZnO inevitably demonstrates a hydrophobic or superhydrophobic behavior depending on its morphology.

**Wettability characterization**

The wettability of the ZnO films was evaluated by CA measurements at room temperature. CA is conventionally defined as the angle between a tangential line along with a liquid–vapor interface and a baseline where the liquid meets a solid surface. The static water CA on the ZnO film was evaluated as 158.2° ± 2°, as seen in figure 3(a), showing the major characteristic property of the superhydrophobic surfaces with water CA larger than 150°. It also amply illustrates that the multi-scaled roughness is essential to superhydrophobicity because only microsized roughness on the ZnO surface renders the CA of 125.8° [45]. In order to thoroughly examine the wettability of ZnO films, the substrate was flipped upside down. The water droplet was tightly pinned on to the surfaces even when inverted, suggesting that strong adhesion exists in normal (perpendicular) direction. It is worth noting that the normal adhesive force is strong enough to firmly grab the water droplet when flipped over as shown in figure 3(b), in which the CA is still as close as 150°, about 148.7° ± 2°. The slight difference of about 2° might result from the pull of gravity when inverted, as reflected by the slightly elongated shape of the water droplet.
Notably, the films show extraordinarily stable hydrophobic performance in more than sixty tests even after four months under ambient conditions, due largely to the fact that the substrate is completely covered with an inorganic material ZnO. Additionally, the single-step synthesis approach is much easier than those multiple-step means reported in the literature, for instance, a two-step synthesis of composite nanofibrous mats of polytetrafluoroethylene/zinc oxide (PTFE-ZnO) developed by Mazhar, et al. [46]. Furthermore, the ZnO films yield a much higher water contact angle (148.7°) than Mazhar’s which are 121.55 degrees with the rise in ZnO content up to 20 wt% compared to the pure PTFE mats. The superhydrophobicity of the ZnO films originates from the very high aspect ratio of ZnO nanohairs, as explained above, coupled with the hierarchical structure [47, 48] as discussed below.

As far as the wettability is concerned, two theoretical models are usually adopted to explain the underlying physics. The first model is the so-called ‘Wenzel model’, \(\cos \theta^* = \gamma \cos \theta\), in which \(\theta^*\) is the equilibrium contact angle from Young’s equation on an ideal solid without roughness, \(\gamma\) is the surface roughness defined as the ratio of the actual area to the projected area of the surface and \(\theta\) is the effective contact angle. Wenzel model [49] applies to the rough surface but with chemical homogeneity, describing a surface on which water droplets penetrate the rough structures leading to high adhesive forces. Usually, a moderate CA is achieved on Wenzel surfaces, as revealed in figure 4(a).

The Cassie-Baxter model [50] considers the flat surface but with chemical heterogeneity, written as: \(\cos \theta^* = f_1 \cos \theta_1 + f_2 \cos \theta_2\), where \(\theta_1,2\) and \(\theta^*\) are Young’s angles of different compositions and the effective angle, respectively, \(f_1\) and \(f_2\) are the area fractions of surface components. One of the optimal conditions is that \(\theta_1\) and \(\theta_2\) are as large as possible. If either one of them is air, let’s say, \(f_2\) represents air, then Young’s angle \(\theta_1\) of water on air is 180°. Since \(\cos 180^\circ = -1\), the Cassie-Baxter then takes the simplified form: \(\cos \theta^* = f_1 \cos \theta_1 - f_2\).
Therefore, the ability to capture air pockets inside the surface structures satisfies an optimal condition to achieve a large contact angle. The multi-leveled structure of ZnO films with micro clusters and nanohairs allows the entrapment of air in the interspaces, which perfectly meets the requirement. Mathematically, another condition to optimize the Cassie-Baxter model is that the smaller \( f_1 \) and the larger \( \theta_1 \) of a solid component, the larger effective contact angle \( \theta^* \) would be. On the ZnO films, nanohairs as protrusions drastically decrease the contact area of a water droplet, leading to a nearly spherical droplet when placed upright. Thereby nanohairs as protrusions minimize \( f_1 \). As analyzed above, due to the Wurtzite ZnO structure with preferential growth along the c axis, hydrophobicity dominates, allowing for a larger \( \theta_1 \). It turns out that the ZnO films have all the prerequisites for superhydrophobicity, which are the multi-level structure entrapping air bubbles, the unique geometrical configuration to reduce the contact area of a water droplet, and the intrinsic hydrophobic property of ZnO. Therefore, super-hydrophobicity was achieved on ZnO films with a CA larger than 150°.

The Cassie-Baxter model, as sketched in figure 4(b), can well interpret the super-hydrophobicity of ZnO films. However, it only indicates the adhesion along the shear direction is ‘slippery’ [51] and does not disclose any information about the normal adhesive force on surfaces. Therefore, it would be quite incomplete to explain the entire phenomenon solely based on the Cassie-Baxter model.

The coexistence of Wenzel and Cassie-Baxter states is called metastate, or Cassie impregnating state or partial wetting model, in which the features of both states are partially inherited as shown in figure 4(c). As the fraction of the solid component ZnO of microclusters and nanohairs increases, the surface composition reaches an ideal value wherein a droplet placed on the surface balances on the solid surface bridging the air pockets thereby giving rise to the superhydrophobic nature. Despite the super-hydrophobic comportment of ZnO films, the surfaces lack the self-cleaning property, meaning the ZnO films behave Wenzel-ly with high adhesive forces. Intensifying scientific investigation has been executed to explore the fundamental physics of the adhesive, which isolates the van der Waals force as the primary source of adhesion [52]. The roughness of microscale clusters of a ZnO surface, which is analogous to that of microstructures on surfaces of gecko’s toes, enables the system to make intimate surface contact with water droplets, leading to short-range van der Waals interactions [53]. Therefore, strong and intimate surface contact, as a result of van der Waals forces, allow for enough normal adhesion to hang a water droplet from an inverted surface. On the other hand, the nanoscale roughness of the ZnO films, can further strengthen the van der Waals forces and increase the normal adhesion through a contact splitting phenomenon [52], exactly similar to the counterparts on gecko’s feet, in which van der Waals dispersion forces are the primary mechanism of adhesion [54].

Overall, the system consists of microclusters and nanohairs on the ZnO platforms. The microclusters ensure sufficient short-distance interactions for the normal adhesion and the platforms provide the bulk scale conformity necessary to adhere to rough or contoured surfaces and superhydrophobicity.

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Figure 4. The schematic diagram for Wenzel, Cassie-Baxter, and Partial Wetting models.

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**Figure 4**. The schematic diagram for Wenzel, Cassie-Baxter, and Partial Wetting models.
Conclusions

In closing, a facile one-step synthesis approach was developed to prepare multilevel structured ZnO films with microclusters and nanohairs. The XRD measurements revealed that the preferential growth direction of ZnO nanohairs is the (002) direction, and the very high aspect-ratio of ZnO nanohairs minimizes the area of the high potential (002) surface. The low surface potential and the large roughness caused by hierarchical structure leads to the superhydrophobicity of the ZnO films, which can be explained with the Cassie impregnating model or partial wetting model. The sufficient short-distance interactions for the normal adhesion are ensured by the microclusters, while the overall ZnO platforms with unique geometrical configuration and chemical composition provide the bulk scale conformity necessary for superhydrophobicity and high adhesion for rough or contoured surfaces. Meanwhile, the superhydrophobic ZnO films exhibit exceptional durability due to its pure inorganic material. Compared with other hydrophobic ZnO coatings, the obtained ZnO films demonstrate many advantages, like the single-step ease synthesis route at low cost which promises for mass scalability, their exceptional superhydrophobicity and phenomenal durability.

Declaration

There is no conflict of interest to declare.

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