

Stable Superhydrophobic Surface via Carbon Nanotubes Coated with a ZnO Thin Film

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We report the formation of a stable superhydrophobic surface via aligned carbon nanotubes (CNTs) coated with a zinc oxide (ZnO) thin film. The CNT template was synthesized by chemical vapor deposition on an Fe–N catalyst layer. The ZnO film, with a low surface energy, was deposited on the CNT template by the filtered cathodic vacuum arc technique. Contact angle measurement reveals that the surface of the ZnO-coated CNTs is superhydrophobic with water contact angle of 159° . Unlike the uncoated CNTs surface, the ZnO-coated CNTs surface shows no sign of water seepage even after a prolonged period of time. The wettability of the surface can be reversibly changed from superhydrophobicity to hydrophilicity by alternation of ultraviolet (UV) irradiation and dark storage.

1. Introduction

Liquid-repellent surfaces are attractive for microfluidic applications in biotechnology,¹ waterproof coatings,² and stain-resistant finishes.³ The hydrophobicity of a surface is determined by a combination of its chemical properties and topographical microstructure.⁴ It is well-known that a flat surface with low surface energy tends to exhibit high water contact angle values on the order of 100 – 120° . However, this is insufficient to produce a water repellent or superhydrophobic surface, which requires a water contact angle larger than 150° .⁵ If a surface is rough or microtextured with a low interfacial free energy, the contact angle of water can reach almost 180° and the surface will remain dry.⁵

The superhydrophobic phenomenon has been observed in aligned carbon nanotubes (CNTs)⁶ and ZnO nanorods⁷ owing to their nanostructures. However, the droplets on CNTs were not stable and eventually seeped into the voids after a few minutes.⁸ Therefore, a thin layer of poly(tetrafluoroethylene) (PTFE) has been coated on the CNTs template in order to create a stable superhydrophobic surface.⁸ However, the deposition of PTFE involves complicated precursors. It is of particular important to investigate other low surface energy materials that can deposit by simple deposition techniques.

Being a wide band-gap semiconductor, zinc oxide (ZnO) has been extensively investigated as an optoelectronic material and nanostructured material.^{9,10} Although hydrophobic conductive ZnO coatings can be fabricated by different processes,^{11,12} it is still difficult to achieve superhydrophobicity without any surface modification. The ZnO nanorod array may also inherit the water seepage problem as in the case of CNT array because voids exist in the nanorods.⁸ The use of CNTs as a template is a very effective method to create nanostructures. In this paper we demonstrate the formation of a superhydrophobic surface from a CNT template with a ZnO coating. It is observed that the

water contact angle of the ZnO-coated CNTs reaches a value of 159° , the surface shows no signs of water seepage even after prolonged periods of time. In addition, the wettability of the ZnO-coated CNTs can be reversibly changed from superhydrophobicity to hydrophilicity by alternation of ultraviolet (UV) irradiation and dark storage.

2. Experimental Section

The aligned CNTs were synthesized by chemical vapor deposition on Fe–N-coated Si substrates. The deposition details have been described elsewhere.¹³ The ZnO thin films were deposited on the aligned CNTs by the filtered cathodic vacuum arc (FCVA) technique.¹⁴ High-purity 99.99% zinc was used as the cathode target, and oxygen gas was introduced into the chamber for the formation of ZnO. ZnO thin film was deposited under the following conditions: oxygen gas flow rate was set to 70 sccm, working pressure to 4×10^{-5} Torr, and arc current to 60 A. The thickness of the ZnO film on silicon substrate, measured by a surface profiler, was found to be about 450 nm for a 10-min deposition at room temperature.

The topographical microstructure of the CNTs template and ZnO-coated CNTs was observed by scanning electron microscopy (SEM; JEOL, JSM-5910LV). Detailed study of the microstructure was also carried out by transmission electron microscopy (TEM; JEOL JEM-2010) operating at 200 kV. The TEM sample was prepared by scratching the sample and directly depositing it on a carbon-coated copper grid. The as-deposited ZnO thin film on a flat silicon wafer was measured by SEM and atomic force microscopy (AFM; Digital Instruments). The water contact angle values were acquired on a Dataphysics OCA-20 contact angle system at room temperature in ambient atmosphere. For each measurement, a $0.5 \mu\text{L}$ droplet was dispensed onto the sample under investigation. Superhydrophobicity was identified in cases where the water droplet did not adhere to the surface (i.e., it rolled off). Therefore, the contact angle values were measured by increasing the droplet volume to $5 \mu\text{L}$ and further touching a water droplet toward the underlying

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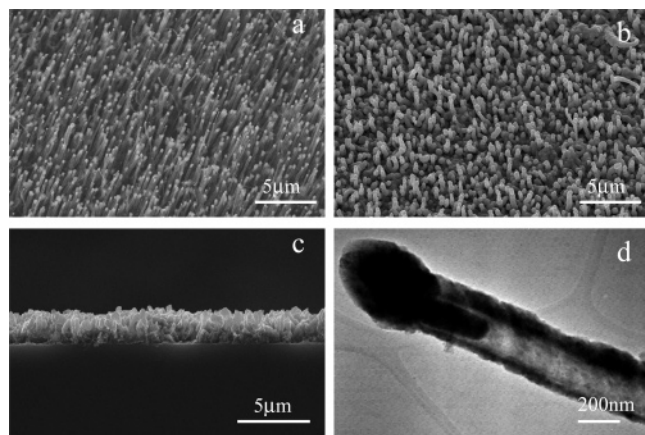


Figure 1. SEM images of (a) as-grown aligned CNT template, (b) topography of ZnO-coated CNTs, (c) cross-sectional view of ZnO-coated CNTs, and (d) TEM image of an individual ZnO-coated CNT.

surface until the water droplet can be pulled down to the sample surface. UV light irradiation was carried out with a UV-ERASER (AT-402 UV EPROM ERASER). The wavelength of UV lamp was 253.7 nm with power density of 8 mW/cm².

3. Results and Discussion

Our group has demonstrated room-temperature deposition of ZnO films with (002) preferential orientation by the filtered cathodic vacuum arc (FCVA) method.¹⁴ The ZnO film is a very smooth, void- and particle-free surface. The SEM image (not shown) does not provide any information on the topographical microstructure. Atomic force microscopy (AFM) was used to observe the surface morphology of the ZnO film. It is observed that the ZnO film deposited on Si wafer is composed of well-faceted grains, with average grain sizes within the range of 40–60 nm. The root-mean-square (rms) roughness of the ZnO film is 1.7 nm, and the peak-to-peak roughness is only 17.1 nm. The shape of the water droplet on the ZnO film deposited on Si wafer has a contact angle of 103° (Figure 2a). The surface is hydrophobic with an ultralow surface roughness. Therefore, it is the low surface energy of the ZnO films that is responsible for the hydrophobic properties. This is consistent with the hexagonal wurtzite structure of ZnO, with their *c*-axis perpendicular to the substrate surface having the lowest surface energy, compared with other orientations of ZnO films.^{7,11,12}

Figure 1a shows the SEM image of the aligned CNTs template grown on an Fe–N catalyst. It is observed that the average diameter and length of the CNTs are 250 nm and 2 μm, respectively. The sample has a relatively low areal density of 3×10^8 CNTs/cm², which is attributed to the selective growth of CNTs at the grain boundary of the Fe–N catalyst layer.¹³ An array of such a low areal density CNT template exhibits superhydrophobic properties, with a water contact angle of 146° (Figure 2b). But the water droplet is not stable and eventually disappears after more than 10 min. As reported by Lau et al.,⁸ the eventual penetration of the water droplet on the low areal density of nanotubes surface is due to a hydrophilic surface of the nanotubes graphitic surface (a graphite material contact angle of 84–86°). Therefore, the low surface energy of ZnO film deposited on the CNT template makes it possible to build a stable superhydrophobic surface by combining the nanostructures inherent in the aligned CNTs template.

Figure 1b,c shows the SEM images of the topography and cross-sectional view, respectively, of aligned CNT template after being coated with a 450 nm thick ZnO film. It is observed that

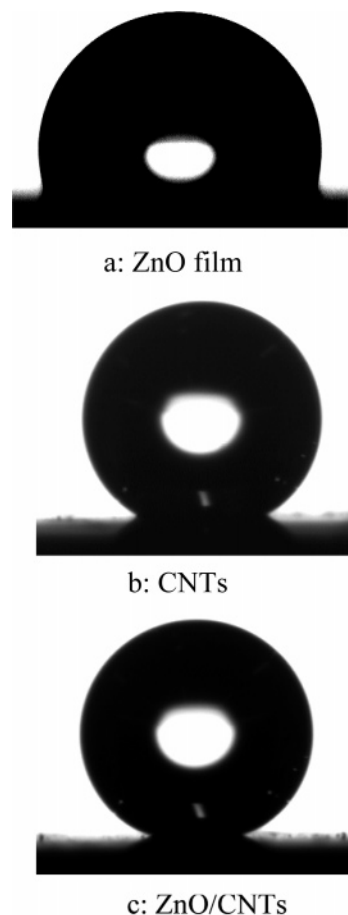


Figure 2. Photographs of water droplet shape on (a) ZnO thin film, (b) as-grown CNTs, and (c) ZnO-coated CNTs.

the nanotube feature is lost. The ZnO coating on the CNTs template is composed of grains of 400–500 nm in diameter. A protruding feature with hundreds of nanometers in height has been formed, where CNTs are encapsulated by the ZnO. In addition, the ZnO is filled in the space between the individual nanotubes as shown in Figure 1c. Figure 1d shows the TEM image of an individual ZnO-coated CNT. It is clearly seen that ZnO is coaxially coated on the CNT where ~450 nm and ~100 nm thick ZnO is on the tip and sidewalls of the CNT, respectively. A metal catalyst can also be observed near the tip of the CNT. The ZnO coating reduces the surface roughness of the CNTs template but maintains the nanostructures by the formation of protrusions. Modification of the CNTs template by the deposition of a ZnO thin film increases the water contact angle to 159° (Figure 2c). In addition, unlike the CNTs template, the ZnO-coated CNTs show stable superhydrophobicity. Figure 3 shows the time dependence of water contact angle for the CNTs templates with and without ZnO coating. It is observed that the water contact angle of the CNTs template decreases linearly with time, from an initial value of 146° to 0° within 15 min. But the contact angle of ZnO-coated CNTs remains constant, showing a stable superhydrophobicity (contact angle > 150°). Since ZnO fills in the gaps between CNTs, it ensures water will not seep into the CNTs.

Sun et al.¹¹ have demonstrated the photoinduced surface wettability conversion phenomenon on both TiO₂ and ZnO thin films. UV illumination can decrease the water contact angle of ZnO film from 109° to 0°, meaning that hydrophobic ZnO can be switched to a highly hydrophilic surface.¹¹ Here, we investigated the UV illumination effect on the superhydrophobic ZnO-coated CNTs. Upon UV illumination for 5 h, the water

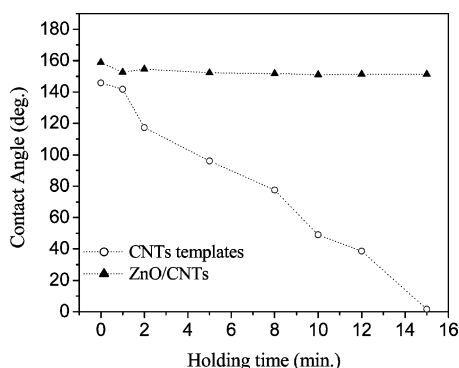


Figure 3. Time dependence of water contact angle for aligned CNT template with and without ZnO coating.

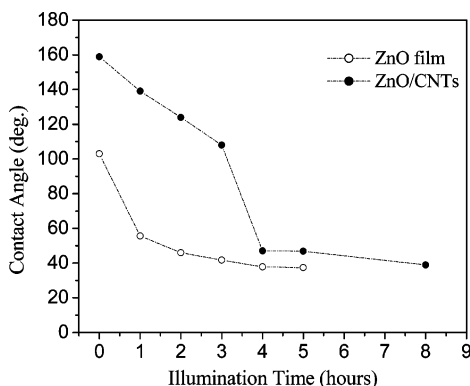
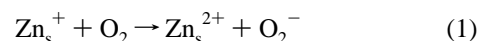


Figure 4. UV exposure time dependence of water contact angles for the ZnO film on the CNT template and Si wafer.

contact angle is reduced to about 46° , indicating that the wettability changes from superhydrophobicity to hydrophilicity. After UV illumination, the samples were kept in the dark for about 12 h; the superhydrophobicity of the ZnO-coated CNTs template is recovered to the contact angle before UV illumination (i.e., 159°). The recovered superhydrophobic surface can be converted to the hydrophilic state again by exposing the films to UV light. Figure 4 shows the UV exposure time dependence of the water contact angles of ZnO film on the CNTs template and Si wafer. It is found that the water contact angle of ZnO-coated CNTs slowly decreased from 159° to 108° after 3 h of UV irradiation and then rapidly decreased to 46° by extending one more hour of irradiation. After that, the water contact angle is reduced only slightly with prolonged periods of UV exposure. It is noteworthy that the photoinduced surface wettability conversion phenomenon of the ZnO-coated CNTs showed behavior similar to that of the ZnO film reported by Sun et al.¹¹ however, the minimum water contact angles as well as the superhydrophobic-to-hydrophilic conversion rates of the ZnO-coated CNTs are different, although higher UV intensity (8 vs 2 mW/cm²), shorter wavelength (253.7 vs 365 nm), and longer illuminated time (5 h vs 20 min) were used in our experiment. These differences may be attributed to surface chemical states of ZnO films, which is strongly dependent on deposition method. It suggests that ZnO films produced by the FCVA technique exhibit less surface defective sites as compared to the spray pyrolysis method.¹¹ The wettability of a surface is primarily determined by its chemical composition and roughness.^{4,5} UV irradiation can only change the chemical states of the surface, which promote water droplets to dissociatively absorb on them.¹¹ The UV illumination generates electron-hole pairs in the ZnO film. Some of the holes can react with lattice oxygen, leading to the formation of surface oxygen

vacancies; while some of the electrons react with lattice Zn^{2+} to form Zn_s^+ , surface trapped electron sites. Zn_s^+ tends to react with oxygen molecules adsorbed on the surface. The formation process of Zn_s^{2+} is represented by



Water molecules may coordinate into the oxygen vacancy sites, which leads to dissociative adsorption of the water molecules on the surface. The process gives rise to increased water adsorption on the illuminated ZnO-coated CNTs.

As shown in Figure 4, the minimum water contact angle of ZnO-coated CNTs after UV irradiation is about 38° , not sufficient to be classified as superhydrophilic. The wettability of the ZnO-coated CNTs can be reversibly changed from superhydrophobicity to hydrophilicity by alternation of ultra-violet (UV) irradiation and dark storage. In fact, the water contact angle of the ZnO coated on the Si wafer is changed from 103° to 37° after 5 h of UV illumination. The superhydrophobic surface needs longer illumination time (i.e., 8 h) to reach the water contact angle of 37° ; this may be due to the difference in functional surface area. It suggests that the photoinduced wettability conversion is independent of its surface structure but depends on its surface chemical composition. Further experiment is needed to verify this point.

Conclusions

We have demonstrated the formation of a stable superhydrophobic surface via aligned carbon nanotubes coated with a ZnO thin film. ZnO-coated CNTs possess the nanofeatured topography inherent in the aligned CNTs template and the low surface energy of ZnO film so as to achieve a stable superhydrophobic surface. Reversible superhydrophobicity to hydrophilicity transition of ZnO-coated CNTs is observed by alternation of UV irradiation and dark storage. On the basis of this study, the superhydrophobic surface from nanostructure materials may have potential applications in microfluidic devices.

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