

Fabrication of Zinc Oxide/Polydimethylsiloxane Composite Surfaces Demonstrating Oil-Fouling-Resistant Superhydrophobicity

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ABSTRACT A novel approach is described for preparing anti-oil-fouling superhydrophobic surfaces. These are produced via the coating of textured hydrophobic zinc oxide on polydimethylsiloxane films to form composite coatings. The surfaces showed superhydrophobic as well as superoleophilic wetting with measured contact and sliding angles for water near 160° and less than 5° , respectively, and contact angles of less than 5° for dodecane. It is demonstrated that subsequent to the fouling of structured surfaces with significant levels of an alkane liquid (oil), the oil is rapidly self-removed, restoring superhydrophobic behavior. Furthermore these protective surfaces can be thermally regenerated for repeated use. This approach is distinct from those reported previously, which rely on expensive fluorochemicals to produce superamphiphobic surfaces. It is believed that the presented approach holds promise in the design of practical anti-oil-fouling superhydrophobic technology.

KEYWORDS: superhydrophobic • self-cleaning • oil fouling • PDMS • superoleophilic • and ZnO

INTRODUCTION

Superhydrophobic surfaces, those exhibiting a static contact angle (CA) with water greater than 150° and a sliding angle (SA) less than 5° , are of high scientific and economic interest (1–14). This interest is encouraged by the super water repellency demonstrated by natural entities such as various leaves (lotus, rice, taro, etc.) (15), butterfly wings (16), mosquito eyes (17), and water strider legs (18). It is now widely held that the key elements of surfaces that promote superhydrophobic states include chemical composition and micro-nano-hierarchical texture. By mimicking the surface structures possessed by these examples on hydrophobic materials, artificial superhydrophobic behavior has been demonstrated, which holds promise for use in industrial applications (1–14). A major shortcoming of both natural and fabricated superhydrophobic surfaces is their susceptibility to oil fouling. Accompanying the engineered ability of these surfaces to repel water is a tendency to interact strongly with nonpolar or oily liquids, which strongly adhere by penetrating into textured interfaces (19). The oil is difficult to remove and negates the superhydrophobic behavior of the affected surface (19). Figure 1 shows an example of this. The image on the left (Figure 1a) is that of water droplets placed on freshly cut tulip leaves (20–22). On the right (Figure 1b) is an image of water droplets placed on the same surface after it had been fouled with dodecane. A clear distinction can be made in the water repellency provided between the clean region and those fouled by the oil.

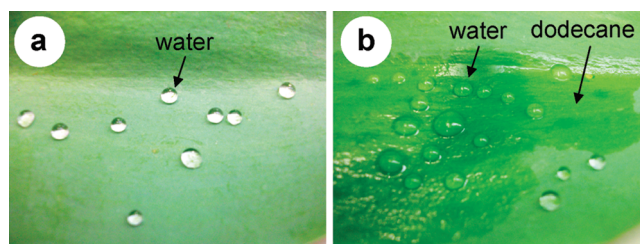


FIGURE 1. Photographs of water droplets on (a) a fresh cut tulip leaf; (b) the same leaf surface fouled by dodecane.

Several researchers have explored artificial super-amphiphobic (both superhydrophobic and superoleophobic) surfaces for mitigating this issue. Jiang et al. grafted a heptadecafluorodecyltrimethoxysilane ($\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$) layer to aligned carbon nanotube (ACNT) surfaces to generate a modified ACNT film showing both superhydrophobicity and superoleophobicity (23). Xie et al. achieved super-amphiphobic films by mixing fluorine-end-capped polyurethane (FPU) and poly(methyl methacrylate) (PMMA), which phase separate forming a micro-nano-binary structure (24). More recently Darmanin and Guittard synthesized fluorinated 3,4-ethylenedioxyppyrrrole (EDOP) and 3,4-propylenedioxyppyrrrole (ProDOP) monomers and their corresponding electrodeposited polymers (25). Only the fluorinated EDOP film demonstrated super-amphiphobic behavior along with extremely low hysteresis and SAs. The fluorinated ProDOP provides only superhydrophobicity with no SA. Although these artificial super-amphiphobic surfaces resist oil fouling, they require use of costly fluorochemicals to achieve the low surface tensions necessary. Furthermore, the preparation process is restrictive because not all treated micro- or nanostructured surfaces will provide superoleophobic behavior (25).

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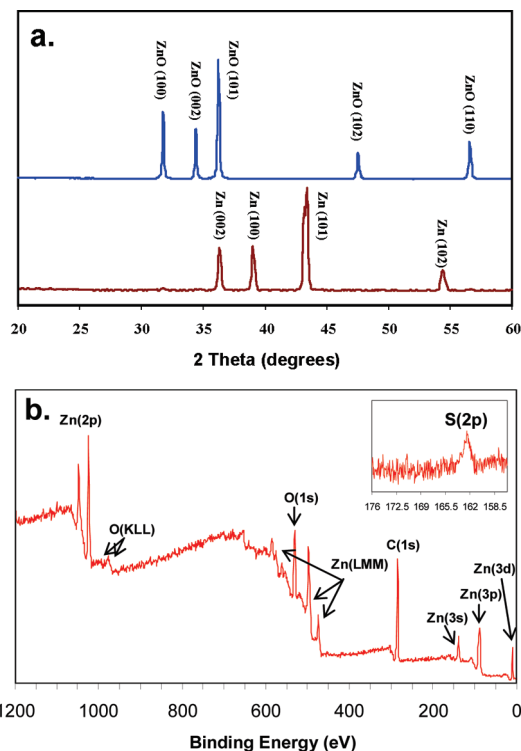


FIGURE 2. (a) XRD spectra of zinc and generated zinc oxide demonstrating conversion to ZnO; (b) X-ray photoelectron spectra (XPS) of the ODT-modified ZnO powder coating. (Inset) spectra for the S(2p) region of samples coated with ODT. The S(2p) peak for the thiolate structure can be clearly seen at ~ 162.5 eV, confirming the presence of an ODT monolayer.

In this paper, a simple yet novel approach is outline for maintaining superhydrophobic behavior in the presence of oil contamination. This is achieved through the use of a composite structure comprised of hydrophobized zinc oxide (ZnO) powder cast on a polydimethylsiloxane (PDMS) film. As expected, the textured ZnO coating expresses superhydrophobicity ($CA_{\text{water}} \approx 160^\circ$ and $SA < 5^\circ$) as well as superoleophilicity ($CA_{\text{oil}} < 5^\circ$) (26–31). When dodecane is added to the composite surface, it is quickly drawn into the texture of the surface. However, within moments, the superhydrophobic wetting behavior returns. For example, water droplets placed on surfaces 30 seconds subsequent to fouling demonstrated a $CA_{\text{water}} > 150^\circ$ and $SA < 5^\circ$. This approach is distinct in its control of oil contamination, as it does not involve formation of a superamphiphobic surface, and it is practical in that the use of expensive fluorochemicals is not required.

RESULTS AND DISCUSSION

Hydrophobized ZnO particles were generated and textured by reacting zinc powder (5 wt %) for 24 h with 30 wt % H_2O_2 adjusted to a pH of approximately 3 using formic acid (32). Particles are isolated through filtration, rinsed with DI water to remove residual chemicals and characterized via X-ray diffraction (XRD). Figure 2a shows the XRD spectra of products before and after the modification, which indicates complete conversion from zinc (Zn) to ZnO. (Peaks at 36.5 , 39 , 43 and 54.5° correspond to Zn (002), (100), (101), (102) planes, whereas peaks at 32 , 33 , 37 , 47.5 , and 56°

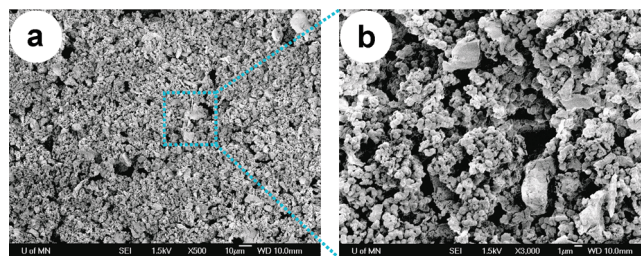


FIGURE 3. Field-emission scanning electron microscopy (FESEM) images of nano-textured hydrophobized ZnO coated on a PDMS substrate including (a) an overview and (b) a magnified view.

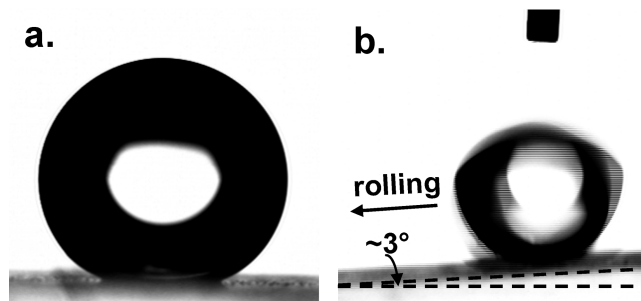


FIGURE 4. Images of water droplets on $ZnO_{\text{coating}}/PDMS_{\text{substrate}}$ composite surfaces including (a) an untitled surface for which a static water CA of $\sim 160 \pm 2^\circ$ was measured, and (b) a surface tilted by $\sim 3^\circ$, which induced drop rolling.

correspond to ZnO (100), (002), (101), (102), (110) planes.) Guo et al. have reported that ZnO surfaces can be made hydrophobic through the generation of an octadecanethiol (ODT) monolayer (33). In their work, water CAs as high as $\sim 99.8^\circ$ were obtained for ODT-modified flat ZnO surfaces (33). Here, generated ZnO powder is immersed for 24 h in a 1 mM solution of ODT in ethanol. ZnO powders were then characterized by X-ray photoelectron spectroscopy (XPS) to confirm the presence of an ODT monolayer (Figure 2b).

The microstructure of the synthesized ZnO was investigated using field emission scanning electron microscopy (FESEM). Suspended particles were coated and dried on a PDMS film (monomer:crosslink = 10:1 in mass; size: 1.5 cm (length) \times 1.5 cm (width) \times 0.2 cm (thickness)) (Figure 3). Visually, hydrophobized ZnO coatings appeared uniform (Figure 3a). Magnified images (e.g., Figure 3b) reveal the nano-structure responsible for inducing superhydrophobic behavior. This is evident from Figure 4a, which shows an image of a water droplet placed on a generated sample: water CAs as high as $160 \pm 2^\circ$ were measured for the samples. Moreover, water droplets were observed to easily roll down sample surfaces when titled 3° (Figure 4b) consistent with Cassie and Baxter superhydrophobic behavior in which drops are suspended atop the structured surface.

To better understand the behavior of the hydrophobized ZnO coatings, theoretical considerations are necessary. In Cassie and Baxter wetting mode (34), water CA on the structured ZnO surface (θ_r) can be expressed as

$$\cos \theta_r = f_1 \cos \theta - f_2 \quad (1)$$

Here θ and θ_r are the water CAs for the flat, untextured hydrophobized ZnO surface and its nano-structured form,

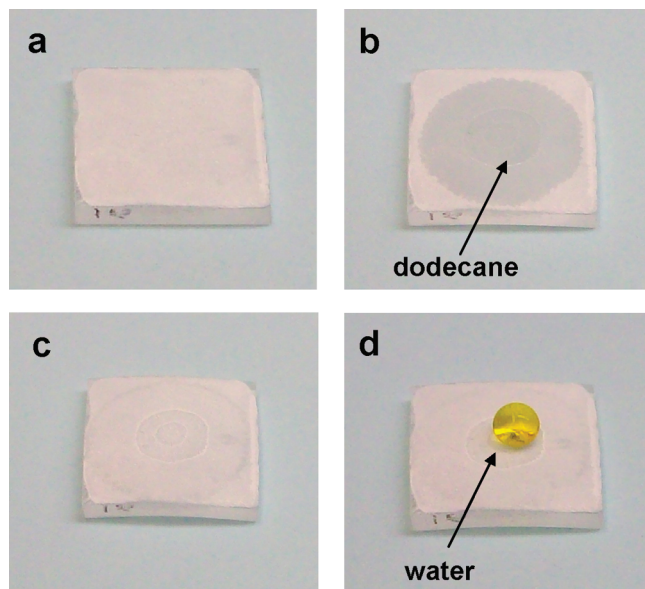


FIGURE 5. Photographs demonstrating the anti-oil-fouling property of ZnO_{coating}/PDMS_{substrate} composite coatings including (a) hydrophobized ZnO coating on a PDMS substrate; (b) the spreading of a dodecane droplet (0.5 μ L) on the coating surface; (c) this droplet after 15 s, showing its near complete removal; and (d) the placement of a water droplet on the coating surface after 30 s, demonstrating the recovery superhydrophobicity.

respectively, and f_1 and f_2 are the area fractions of the ZnO surface and air in contact with water, respectively (i.e., $f_1 + f_2 = 1$). From eq 1, it can be seen that increasing f_2 increases θ_r . In other words, as the amount of air under the contact line is increased the more hydrophobic it appears. According to eq 1, the value of f_2 of the nano-structured ZnO surface is calculated to be 0.927 (33), indicating that the fraction of air trapped on the surface is primarily responsible for the superhydrophobic behavior.

The Wenzel wetting mode can be expressed as

$$\cos \theta_r = r \cos \theta \quad (2)$$

where r ($r \geq 1$) is surface roughness with $r = 1$ for smooth surfaces (35). This equation indicates high roughness may turn an oleophilic surface to superoleophilic. When dodecane drops ($\sim 0.5 \mu$ L) are placed on the ZnO coated samples, they spread within moments (within 3 s) to CAs of less than 5° . That is, the hydrophobized ZnO coating, which demonstrates superhydrophobic behavior, also shows superoleophilicity (Figure 5a, b). Subsequent to forming a low-contact-angle drop, the oil layer disappears from the surface (Figure 5c). This occurs within a timeframe of about 15 s and is followed by the return of superhydrophobic wetting behavior (Figure 5d). Figure 6a shows the image of a water droplet placed on the dodecane-fouled surface (30 s after oil addition). The CA for the water is again high, $160 \pm 2^\circ$, and water droplets easily roll from the coating surface when the sample is tilted 3° (Figure 6b). These results indicate that the superhydrophobic ZnO_{coating}/PDMS_{substrate} surfaces are resilient with regard to oil fouling. A video has been included as part of the Supporting Information showing how quickly the

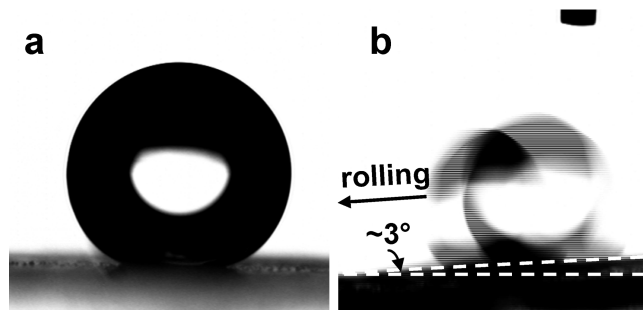


FIGURE 6. Images of water droplets placed on (a) level and (b) tilted ($\sim 3^\circ$) dodecane-contaminated superhydrophobic ZnO_{coating}/PDMS_{substrate} composite surfaces. Tests were performed 30 sec. after applying dodecane and demonstrate the return of superhydrophobic wetting behavior shown in Figure 4, i.e., a water CA of $\sim 160 \pm 2^\circ$ and the induced rolling of the water drop down the tilted surface.

surface can self-remove the oil layer and recover its superhydrophobic behavior.

The mechanism involved in the anti-oil-fouling performance of these structures appears to be the swelling of the underlying PDMS substrate, which rapidly draws oil from the structured coating. Factors controlling the effectiveness of this anti-oil-fouling property likely includes: the efficiency to which the oil wets the coating and ability of the polymeric substrate to absorb the oil. Dodecane has a strong tendency to wet the prepared hydrophobized coatings, spreading rapidly (< 3 s) to form a thin oil layer.

Evidence for the importance of the underlying substrate to absorb oil can be demonstrated by designing similar composite coatings using an alternative polymer base. For example, when hydrophobized ZnO is cast on a polyethylene terephthalate (PET), i.e., ZnO_{coating}/PET_{substrate}, a superhydrophobic coating results, ($CA_{\text{water}} \approx 160^\circ$ and $SA < 5^\circ$) However, an added dodecane layer is visible indefinitely and anti-oil-fouling behavior is lost (see Figure S1 in the Supporting Information). To demonstrate the ability of PDMS to absorb oil, we added a drop of dodecane (0.0060 g) to a clean, flat piece of PDMS, CA was $28 \pm 1^\circ$, which was then placed on an analytical balance. After 1 min, the oil drop was wiped clean from the surface. Upon reweighing, it was found that the mass of the PDMS film had increased by 0.0017 g (accounting for about 25% of the added oil). It was also observed that the oil absorption produced a small change in the shape of the PDMS film due to the swelling (36, 37) (see Figure S3 in the Supporting Information). This measurement was repeated with PDMS of cross-linking densities of 5:1 and 20:1 (in mass), with similar results (e.g., oil absorption of ~ 25 and $\sim 29\%$, respectively). It was also found that the effects of the oil uptake can be reversed completely by heating the swollen samples at 65°C for 1 h, indicating the formed structures are reusable after relatively minor treatments. It is likely that similar results will be observed for other alkane oils and many common organic solvents. This assertion is based on the high swelling ratio of PDMS for a variety of organic liquids such as xylene, chloroform, toluene, *n*-pentane, *n*-heptane, etc. (38). Dodecane was selected here for its low vapor pressure, which helped limit error due to evaporation.

CONCLUSIONS

In summary, a novel approach for preparing anti-oil-fouling structures was introduced involving the coating of textured hydrophobic ZnO on PDMS films. These composite surfaces are shown to be superhydrophobic as well as superoleophilic. It is demonstrated that significant levels of dodecane can be self-removed by the ZnO_(coating)/PDMS_(substrate) surfaces within 30 s, and superhydrophobic behavior is recovered. This approach is distinct from those reported previously, which rely on expensive fluorochemicals to produce superamphiphobic surfaces. It is believed that the presented approach holds promise in the design of practical superhydrophobic technology.

EXPERIMENTAL SECTION

In a 50 mL flask, 1.0 g of zinc powder (325 mesh, purity 99.1 % from Ebay) was mixed with 19.0 g of a 30% aqueous H₂O₂ solution (Fisher Scientific, Pittsburg, PA) and the pH value was adjusted to ~3 with formic acid (Fisher Scientific, Pittsburg, PA). The mixture was continuously mixed with a magnet stirring bar for 24 h under ambient conditions followed by centrifugation and removal of the aqueous supernatant. The pellet was then rinsed multiple times with DI-water and mixed with 1 mM octadecanethiol (ODT, from Aldrich, St. Louis, MO) solution in ethanol for 24 h. After centrifugation, the solid was rinsed with ethanol and dispersed into 15.0 g DI water to form the ODT-treated ZnO suspension. Coatings were produced by blending the suspension and placing drops of sizes ~0.3–0.35 g/cm² on prepared PDMS substrates (Sylgard 184 Silicone Elastomer) obtained from Dow Corning Corporation (Midland, MI), which were cured in a 65 °C oven for 2 h prior to use. The coatings were then dried in a 100 °C oven for 24 h.

Zn and the generated ZnO were characterized by X-ray diffraction (XRD), and the coatings were characterized using X-ray photoelectron spectra (XPS), contact angle (CA) measurements, and the field-emission scanning electronic microscope (FESEM). X-ray diffraction was conducted on Bruker-AXS (Siemens, Munich, Germany) D5005 operated at a voltage of 45 kV with a current density of 40 mA and scanning range was from $2\theta = 20\text{--}60^\circ$ at a scan speed of 0.048°/s. The XPS experiments with varying tilt angles were measured with a VG ESCALAB MKII (West Sussex, UK) instrument at room temperature by using an AlK α monochrom ($h\nu = 1486.6$ eV) at 14 kV and 20 mA. Contact angles were determined with a Krüss (Krüss GmbH, Germany) DSA10-MK2 contact angle measurement system at ambient temperature. Deionized water with droplet volumes of 10 μ L and dodecane (purity >99%, Acros Organics, Morris Plains, NJ) with droplet volumes of 0.5–1 μ L were used as probe liquids. Average CA values were obtained by measuring the same sample at 3 different positions. Microstructures of surfaces were investigated with a JEOL (Tokyo, Japan) 6500 scanning electronic microscope operating at 20 kV. All photography and video were captured by a Kodak Easyshare M7.1 digital camera.

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Supporting Information Available: Photographs are provided of dodecane on a ZnO/PET composite surface, dodecane on pure PDMS, and evidence of PDMS swelling by

dodecane (PDF); real-time video is provided showing the fouling of the ZnO/PDMS composite surface by dodecane and recovery of its superhydrophobic wetting behavior (WMV). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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