

Research Article

Improving the Hydrophobicity of ZnO by PTFE Incorporation

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The objective of the present study is to obtain a zinc oxide- (ZnO-) based superhydrophobic surface in a simple and cost-effective manner. Chemical immersion deposition being simple and economical has been adopted to develop modified ZnO coating on glass substrate. Several modifications of ZnO like treatment with alkanolic acid (stearic acid) and fluoroalkylsilane to tune the surface wettability (hydrophobicity) were attempted. The effect of thermal treatment on the hydrophobic performance was also studied. It was observed that thermal treatment at 70°C for 16 hrs followed by immersion in stearic acid resulted in high water contact angle (WCA), that is, a superhydrophobic surface. Thus, a modified ZnO superhydrophobic surface involves the consumption of large amount of electrical energy and time. Hence, the alternate involved the incorporation of low surface energy fluoropolymer polytetrafluoroethylene (PTFE) in the ZnO coating. The immersion deposited ZnO-PTFE composite coating on modification with either stearic acid or fluoroalkylsilane resulted in a better superhydrophobic surface. The coatings were characterized using Scanning Electron Microscope (SEM) for the surface morphology. It was found that microstructure of the coating was influenced by the additives employed. A flower-like morphology comprising of needle-like structure arranged in a radial manner was exhibited by the superhydrophobic coating.

1. Introduction

Superhydrophobic surfaces (water contact angle $>150^\circ$) are gaining importance in industrial applications and academia due to their unique properties like self-cleaning, deicing, antisticking, and anticontamination. Some of the applications include self-cleaning paints, transparent antireflective coatings, self-cleaning glass, and wiperless windshields. In recent times, their usage in aerospace sector is also being explored, particularly in the tail and wings of the aircraft to reduce drag and thereby improve the efficiency of the engine. Superhydrophobicity can be achieved by obtaining a surface of micro- to nanoscale architecture [1]. Empirical models have been proposed on the basis of experimental data to explain the surface wetting properties and to understand the phenomenon of superhydrophobicity. Interest in this phenomenon increased in 1997 when the origin and the universal principle of “Lotus Effect” in nature were explained by Zhang et al. [1]. Since then, research has been focused on mimicking nature and trying to fabricate such surfaces artificially.

Various methods have been recommended for the fabrication of such a surface. Broadly, they have been classified as top-down approach, bottom-up approach, and a combined approach. Solution immersion process, which is a bottom-up method, has been adopted in the present study. The advantage of this method is that it is simple, economical and can be easily scaled up for large area applications. ZnO has been chosen because of its antimicrobial property, easy availability, and nontoxic nature [2]. Also it has other properties like photocatalytic ability, electrical conductivity, UV absorption, and photo-oxidizing capacity for chemical and biological species. Very recently, preparation of cotton bandages with antibacterial properties by immobilizing ZnO nanoparticles on the fabric surface has been reported [3]. Considerable work has been carried out on the immersion deposition of ZnO [4–12]. Shinde et al. have reported the structure, optical and electrical properties of heat-treated ZnO [4]. Similar aspect of Sr-doped ZnO film has also been studied [5]. The effect of thermal desorption of stearic acid on the superhydrophobic performance of ZnO has been reported by Saleema and Farzaneh [6]. ZnO nanorods have

been synthesized by chemical route by some investigators [7]. Yin and Sato have reported novel superstructures of ZnO, namely, nanoscrew and nanodisk obtained from the solution route [8]. Other modified superhydrophobic surfaces based on Cu, Ag, Co, Ni created through solution immersion process have also been reported [13–17]. In the present study, solution immersion deposited ZnO coating has been subjected to different modifications like heat treatment, immersion in alkanolic acid (stearic acid), combination of heat treatment and immersion in alkanolic acid, and immersion in fluoroalkylsilane. Stearic acid had been adopted as Wu et al. had reported that octadecanoic acid (C18 acid, stearic acid) imparted higher hydrophobicity compared to other acids of different chain lengths [9]. The influence of polytetrafluoroethylene (PTFE) on the hydrophobic nature was also studied by preparing ZnO-PTFE composite coating by immersion route. PTFE was chosen as it is a fluoropolymer with very low surface energy. The water contact angle of smooth PTFE film is about 108° , and by the axial extension of the crystals the water contact angle increases beyond 150° [18]. The PTFE-based coatings were also modified with alkanolic acid and fluoroalkylsilane. Thus, in this study, the investigators have attempted to improve the superhydrophobic behaviour of ZnO by PTFE incorporation, and a comparison with modified ZnO in terms of their microstructure and wettability behaviour has been made.

2. Materials and Methodology

ZnO was deposited on a glass substrate by immersion in a solution containing 30 g L^{-1} zinc nitrate hexahydrate and 53.3 mL L^{-1} ammonium hydroxide solution (25%). The chemical etching of the substrate was carried out to induce surface roughness. Surface roughness plays an important role in determining the wetting behaviour of solid surfaces [19]. The etchant and etching time was standardized. HF:HNO₃ mixture in the ratio 1:3 for a duration of 3 sec was adopted to obtain uniform ZnO coating on glass. The immersion time and temperature were also standardized. Deposition temperature of 70°C and an immersion time of 2 h after initiation of precipitate formation were employed. The as-prepared ZnO coatings were subjected to modifications such as heat treatment at 350°C (for 2 h and 4 h) and immersion in alkanolic acid-octadecanoic acid (stearic acid). The various concentrations of the acid solution in acetone used were 0.002 M, 0.01 M, 0.06 M, and 0.10 M. The other modifications included heating of ZnO coating at 70°C for 16 h followed by immersion in alkanolic acid and modification of the coating by immersion in fluoroalkylsilane, 1 wt% FAS-17 solution in ethanol for 1 h. The modified coatings were dried under ambient conditions.

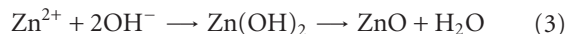
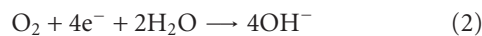
The ZnO-PTFE composite coatings were deposited by dispersing the PTFE (10 mL L^{-1}) emulsion in the zinc nitrate solution, and the deposition was performed under similar conditions as that of ZnO. The composite coating was modified by immersion in 0.002 M stearic acid solution in acetone for 1 h and fluoroalkylsilane in ethanol for 1 h. These modified coatings were characterized for their surface

morphology and wetting behavior, and a comparison with modified ZnO has been made.

Static water contact angles (WCAs) of the coatings were measured using contact angle analyzer, model Phoenix 300 Plus from M/s Surface Electro Optics, Republic of Korea. Tangent fitting mode is used in this instrument for the determination of WCA. The drop volume was $8\text{ }\mu\text{L}$ in this study. WCA is influenced by volume of water droplet and gravity force. Hence, WCA must be measured with the same volume of water droplet. Also, the same fitting method must be used for calculating WCA while comparing superhydrophobicity of different surfaces as explained by Zhang et al. [1]. They found that WCA values from 156° to 179° could be obtained for the same water droplet on a surface depending on different fitting modes such as ellipse fitting, circle fitting, tangent searching, or Laplace-Young fitting. Five measurements of WCA on the coating were taken, and the mean value was reported. The crystalline structure of the coatings was examined by X-ray diffraction (XRD) technique, Model Rigaku D/max 2200 powder diffractometer, using CuK_α radiation of wavelength 0.154 nm. The diffraction patterns were scanned between 20° and 100° in steps of 0.02° at 2 deg min^{-1} scan speed. The surface morphology of the coatings was studied using a scanning electron microscope, SEM Model LEO 440I.

3. Results and Discussion

3.1. Microstructure and Hydrophobicity of Modified ZnO Coatings. X-ray diffraction patterns of as-deposited ZnO coating and modified ZnO coating are shown in Figure 1. The diffraction peaks in Figure 1(a) indicate the presence of major amounts of ZnO with hexagonal wurtzite structure and smaller amounts of zinc hydroxide, Zn(OH)₂. No other characteristic peak was observed for other impurities, and all the peaks are narrow indicating higher crystallinity. The probable reaction mechanism is



Zinc gets oxidized forming zinc cations (1), and oxygen gets reduced producing hydroxyl ions (2). These hydroxyl anions react with zinc cations to form zinc hydroxide (reaction (2)) which under slightly acidic condition transforms to the stable ZnO that is insoluble and appears as white precipitate on the surface [19]. This mechanism can be correlated with the presence of ZnO and Zn(OH)₂ in the diffractogram.

Surface morphology of various modified ZnO coatings is shown in Figure 2. It can be seen from Figure 2(a) that the morphology of as-deposited ZnO coating consists of uniform flower-like pattern. Every flower-like structure is composed of many rods with a sharp tip, and these rods are aligned in a radial pattern from the centre. The growth mechanism can be interpreted as an epitaxial growth wherein the ZnO nuclei initially formed a seed layer. The ammonium ions adsorbed on the surface of the ZnO nuclei promoted

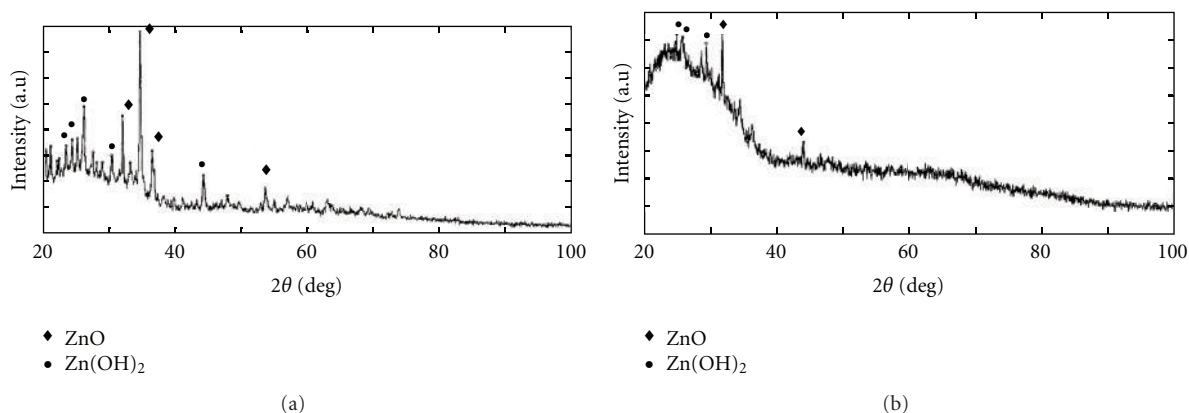


FIGURE 1: X-ray diffractograms of (a) as-deposited ZnO coating and (b) ZnO coating heat treated at 70°C and immersed in stearic acid (0.002 M).

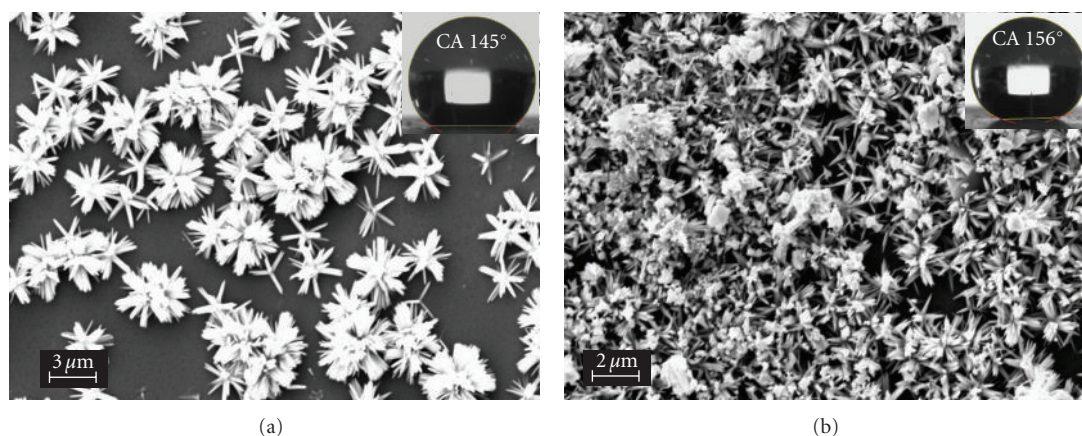


FIGURE 2: Surface morphology of ZnO coating immersed in stearic acid (a), ZnO heat treated at 70°C and immersed in stearic acid (0.002 M) (b). Insets show the profiles of the water droplet on the film surface.

the growth of the crystallites [9, 20]. Similar structure has been reported by Wang et al. for ZnO powder synthesized from ZnSO₄ and NaOH solution [21]. However, Shinde et al. have reported a cone-like structure for ZnO deposited from an alkaline Zn(NO₃)₂ solution [4]. Thus, by varying the alkalinity of the solution, different morphologies can be obtained. Strong alkaline solution results in a structure comprising of discrete nanorods, while a weak alkaline solution produces an assembled nanorod structure [21]. Zhang et al. have also reported the influence of pH on the surface morphology and wettability [19].

ZnO is basically a highly hydrophilic material with WCA < 5°. After heat treatment at 350°C for 2 h and 4 h, the ZnO coatings did not exhibit any change in their wetting behaviour and remained hydrophilic. Hence, their detailed characterization has not been discussed. However, Shinde et al. have reported that the ZnO coating annealed at 350°C for 2 h displayed superhydrophobic nature and its structure appeared as well-defined cones [4]. Thus, the wettability of solid surface is governed by both the chemical composition and the geometrical microstructure of the surface.

ZnO coatings were hydrophobically modified by immersing in varying concentrations of stearic acid for different durations of time, and their WCA values were measured. It was observed that the as-deposited ZnO coating after immersion in 0.01 M stearic acid for 6 days displayed a WCA of 145°. The surface morphology and diffraction pattern of the coating modified with stearic acid was similar to that of the as-deposited ZnO coating. In order to render hydrophobicity to the coating, a prolonged immersion time of 6 days was required. On the other hand, if ZnO coating was heated to 70°C for 16 h and subsequently immersed in stearic acid, superhydrophobicity was achieved in much shorter immersion time. The heat-treated ZnO coating was immersed in stearic acid of different concentrations and for various time durations. It was found that a low concentration of 0.002 M and short immersion time of 30 minutes was optimum to obtain superhydrophobicity. The morphology appears as sword-like nanorods with sharp tips, arranged in a flower-like arrangement (Figure 2(b)). In addition, cluster of flowers grouped over one another was also observed. EDX analysis revealed that the Zn content was slightly lower

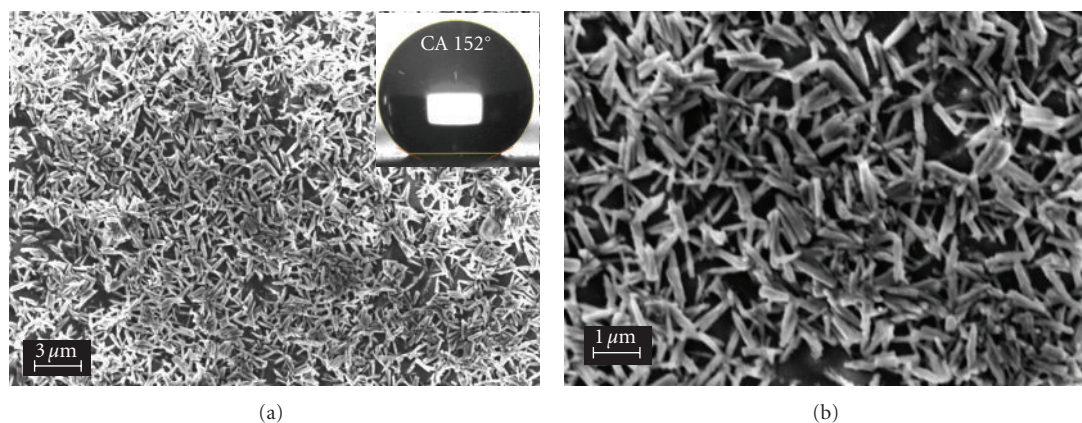


FIGURE 3: Surface morphology of ZnO coating treated with fluoroalkylsilane at 2500X (a) and 5000X (b). Inset shows the image of water drop on the film surface.

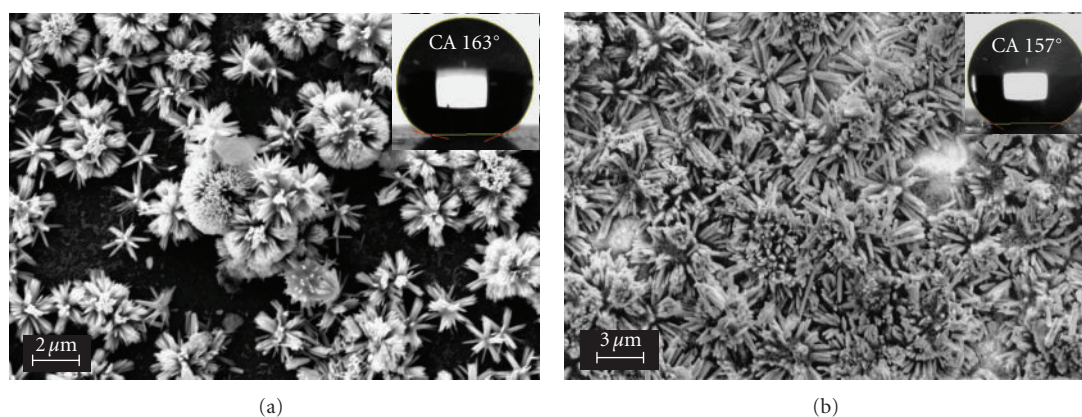


FIGURE 4: Surface morphology of ZnO-PTFE coating treated with stearic acid (a) and fluoroalkyl silane (b). Insets show the image of the water drop on the film surface.

on these clusters (65 wt%) as compared to single flower (72 wt%). Further, a marginal rise in carbon and oxygen content was observed on the floral cluster. This may be due to the contribution from the stearic acid. The X-ray diffractogram shows the presence of ZnO and Zn(OH)₂ (Figure 1(b)). The effect of fluoroalkylsilane modification on the hydrophobic behaviour of ZnO was also studied. The morphology of fluoroalkylsilane-modified ZnO coating is depicted in Figure 3. The structure appears as discrete rods distributed uniformly throughout the surface. The X-ray diffraction studies showed the presence of only Zn(OH)₂.

The wettability of the coatings is expressed as water contact angle, and this angle is inversely proportional to the wettability. Figure 2 shows the water drop profile for (a) alkanolic acid-modified coating, (b) heat-treated followed by alkanolic acid modification and Figure 3 shows the profile of fluoroalkylsilane-modified coating. As-deposited ZnO coating was observed to be hydrophobic, with a WCA of 120°. However, on immersion in 0.10 M stearic acid, an improvement in the hydrophobic behaviour was observed with an enhancement in the contact angle values to 145° (Figure 2(a)). However, a combined treatment of heating

at 70°C and immersion in 0.002 M stearic acid rendered the coating superhydrophobic. It exhibited a contact angle of 156°, and the shape of the water droplet is shown in Figure 2(b). The hydrophobicity imparted by stearic acid can also be attributed to the fact that stearic acid chemically bonded to the surface of Zn²⁺ ions leading to the ZnO surface being covered by a monolayer of organic molecules with their nonpolar tails exposed to air [9]. The fluoroalkylsilane modified ZnO coating also exhibited superhydrophobic behaviour with a moderate reduction in the contact angle values to 152° (Figure 3). The higher contact angle (156°) of the coupled heat treatment and stearic acid modification of ZnO coating may be due to the less air entrapment in the clustered floral structure compared to the rod-like structure of silane-modified coating. Thus, different WCAs are due to the different surface structures. It can also be inferred that fluorosilane imparts higher degree of hydrophobicity (152°) due to its low surface free energy compared to exclusive alkanolic acid treatment (145°).

The above studies showed that superhydrophobic ZnO surface can be achieved, by heating for long hours (16 h) followed by short duration (0.50 h) immersion in stearic

acid. Although the coating is superhydrophobic in nature, a long time was spent to attain this nonwetting property. Hence, an alternative ZnO-PTFE composite coating was produced by solution immersion method.

3.2. Microstructure and Hydrophobicity of Modified ZnO-PTFE Composite Coating. The ZnO-PTFE composite coating was developed in a similar manner as that of ZnO coating, and it was subsequently modified with stearic acid and fluorosilane. The surface morphology of the modified ZnO-PTFE composite coatings is depicted in Figure 4. The surface morphology of stearic acid-modified ZnO-PTFE coating appears as floral structures along with a clustered growth (Figure 4(a)). The EDX studies showed that the clustered structure was rich in fluorine (5 wt% on the cluster and 2 wt% on floral pattern) indicating that it was the contribution from PTFE. The X-ray diffraction studies revealed that the coating comprised of ZnO and Zn(OH)₂. The silane-modified coating exhibited a structure comprising of compactly arranged rod-like structures distributed in a random manner (Figure 4(b)). The diffraction studies showed that the coating comprised of exclusively Zn(OH)₂. It was seen from the wettability test that the contact angle for stearic acid-modified ZnO-PTFE coating is 163° while that for silane-modified coating is 157°. The water drop profiles are depicted in Figure 4. Thus, it is observed that the incorporation of low surface energy PTFE in ZnO helped to improve the hydrophobicity without the necessity of heat treatment or long immersion time. It is also seen that unlike the modified ZnO coating wherein the fluorosilane imparted higher hydrophobicity compared to alkanolic acid, in the case of ZnO-PTFE coating the alkanolic acid imparted higher degree of hydrophobicity compared to fluorosilane. This may be due to the difference in the interaction of PTFE with stearic acid and fluoroalkylsilane. Thus, modified ZnO-PTFE composite helps to obtain a superhydrophobic surface in a simple manner. This can be associated with the interaction between fluorine, the most effective element for lowering the surface free energy, because of its small atomic radius and high electronegativity, and the roughness of the substrate induced by etching.

The superhydrophobic behaviour of modified ZnO films can be explained in terms of the Cassie-Baxter model [22]. According to Cassie-Baxter equation,

$$\cos \theta_C = f_1(\cos \theta_1 + 1) - 1, \quad (4)$$

where θ_C and θ_1 , respectively, are apparent WCA of the corresponding rough and smooth surfaces, f_1 is the surface area fraction of the solid. A water drop on the modified ZnO film only contacts the tips of the clusters and flower-like structures on the rough surface resulting in a large water-air interface. Such composite surface prevents water droplets from penetrating into the cavities, leading to superhydrophobicity. However, in unmodified ZnO films, water penetrates into the gap between the clusters thereby displaying merely a hydrophobic behaviour.

4. Conclusions

ZnO being a widely adopted material to obtain superhydrophobic surface was deposited on glass substrate by immersion deposition method. Some of the modifications adopted by various investigators like alkanolic acid immersion, heat treatment, and fluoroalkylsilane modification were carried out for the ZnO coatings obtained in the present study. The observation made was that ZnO deposition followed by heat treatment at 70°C for 16 hours and immersion in a solution of stearic acid had resulted in a surface with the highest hydrophobicity (CA 156°). The studies conducted also revealed that the modification of ZnO with fluoroalkylsilane imparted superhydrophobicity but to a lesser extent (CA 152°). The prolonged heat treatment time (16 h) can be avoided by the incorporation of a low surface energy PTFE in the ZnO coating. The ZnO-PTFE composite coatings on modification with either stearic acid or fluoroalkylsilane imparted greater superhydrophobicity compared to modified ZnO coatings. It was also seen that the surface morphology of the coating was greatly influenced by the nature of low energy material used for hydrophobic modification.

It was inferred from the morphology and contact angle measurement studies that the incorporation of PTFE in ZnO matrix followed by modification with stearic acid or fluoroalkylsilane produced a superhydrophobic surface in a simple and cost effective manner.

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