Preparation Of Superhydrophobic Zinc Oxide Nanorods Coating On Stainless Steel Via Chemical Bath Deposition

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Abstract. The stearic acid modified zinc oxide nanorod surface was coated with a stainless steel substrate to improve the contact angle and the sliding angle. Facilitated through ZnO seeding on the substrate, the ZnO nanorod was deposited via chemical bath deposition at different precursor concentrations. The surface hydrophobicity was modified by varying concentrations of stearic acid at and submersion time. The contact angle was investigated in relation to the surface microstructure and modification. Results indicate that the density of ZnO nanorods on the substrate surface and stearic acid coverage are prerequisites for improving surface hydrophobicity. Superhydrophobic properties with a contact angle of 162° was obtained for ZnO deposited with 35 mM zinc nitrate and submerged in 8 mM stearic acid for 36 h, which allowed 5 μL water droplets to slide at 3.8°.

Keywords: stainless steel, chemical bath deposition, stearic acid, contact angle.

1. Introduction

Learning from natural properties of the surface of the lotus leaf, any material surface essentially can be modified into a superhydrophobic. Rigorous observations of physical properties of the lotus leaf surface show that there are two important aspects governing its hydrophobicity, which are (1) specific patterning of the surface microstructure and (2) low surface energy against droplets of water. The surface microstructure should provide air trapping under the water droplet and minimize contact area between droplets and surface, whilst the contact surface with droplet should have low energy [1]. By mimicking lotus leaf properties, numerous works have been conducted that modify various solid surfaces to obtain superhydrophobic behavior [2-5]. Material with rough surface structure is suitable for providing air trapping capability with a less
contact area to water droplet. Covering the contact surface area with thin film of low surface energy will enhance water repelling.

Stainless steel (SS) has been widely utilized for construction related works and technological products due to its superior mechanical and physical properties [6]. Stainless steel is an iron based metal containing ~ 18 wt-% chromium and ~ 8 wt-% nickel, and sometimes mixed with small amounts of molybdenum. High chromium content and nickel makes the steel resistant to hazard and chemical environments, and molybdenum improves its resistance to corrosion. There has been a growing interest in utilizing stainless steel in relation with its surface corrosion resistance and hydrophobic property. However, the stainless steel surface is naturally hydrophilic, which required surface modification for particular utilization. Imitating the lotus leaf properties, the stainless steel surface must be microscopically patterned and covered by material with low surface energy.

Up to now, patterning the stainless steel surface was prepared either by engraving its surface or by depositing its micro-nano-texture thin film. Engraving the steel surface includes sand blasting [7], laser ablation [8,9], and wet etching using strong acid solutions ferric chloric acid [10], hydrosulfate acid [11], hydrochloric acid [12]. Depositing thin film with micro-nano-texture surface on steel substrate has been performed with electroless plating of nickel in a bath solution of nickel sulfate and hydrazine [13], electrodeposition of nickel in an aqueous mixed solution of nickel chloride, boric acid and lauryl sodium sulfate [14], spin coating of boehmite thin film from gel containing aluminum tri-sec-butoxide, isopropyl alcohol and ethyl acetoacetate [15], electrodeposition of silica in solution consists of potassium nitrate, tetraethyl orthosilicate, and dodecyltrimethoxysilane [16], electrodeposition of ZnO in mixed solution of zinc chloride and zinc nitrate [17], and spray coating of fluorinated polysiloxane/modified ZnO [18]. Recently, there have been attempts to prepare micro-nano-texture stainless steel surface by combining steel surface patterning and depositing thin film. Motlagh et al. fabricated superamphiphobic surface of stainless steel by surface sandblasted and thin film deposition of silane-encapsulated silica nanoparticles [19]. Meanwhile, Boinovich et al. developed icephobic stainless steel by subsequent process of chemical etch and coat with silica nanoparticles containing hydrophobic agent, leading to the formation of multistructure surface with capability of repelling water even at low temperature [20].

ZnO nanorod was an excellent thin film material with a surface structure that can easily be modified during or post deposition. This material can be deposited on various substrates with different methods [21]. In this study, ZnO nanorod was coated on ZnO seeded chemically etched stainless steel substrate by chemical bath deposition method. Etched steel surface guided to unaligned orientation of ZnO nanorods growth, which lead to a hierarchical surface roughness. Deposition precursor concentration was used to fine-tune the surface microstructure and coverage of ZnO nanorods on the substrate. The surface energy of ZnO nanorods was modified using stearic acid owing its inexpensive and wide technological applications.

2. Materials and Methods

2.1 Materials

Depositions of ZnO nanorods were performed on commercial stainless steel pipe with dimensions of 101.6 mm in diameter and 1.65 mm in thickness. The chemical composition of steel was examined by an Optical Emission Spectrometer (Thermo Scientific, ARL3460). The stainless steel contains wt-%: Fe 69.97, Cr 16.66, Ni 9.67, Mo 2.001, Mn 0.89, Si 0.37, Cu
0.229, V 0.097, W 0.034, P 0.033, Nb 0.016, C 0.014, S 0.007, Sn 0.007, Ti 0.001, and Al 0.001, which is a typical chemical composition of the 316 stainless steel [22]. Zinc acetate dehydrate, zinc nitrate tetrahydrate, diethanolamine (DEA), hexamethylenetetramine (HMT) were obtained from Sigma-Aldrich. Stearic acid (SA), acetone, ethanol and ethylene glycol were purchased from Merck. All chemical substances were used without further purification.

2.2 Preparation of ZnO seed and deposition of ZnO nanorods

The preparation of hydrophobic samples appears in Figure 1. The inner surface of stainless steel pipe was etched with strong acid solution forming a rough surface to facilitate heterogeneous ZnO growth. ZnO nanorods growth on stainless steel substrate was guided by ZnO seeds deposited on an etched stainless surface [23]. The Chemical Bath Deposition (CBD) method was used to deposit ZnO nanorods, and the surface of ZnO nanorods were modified by stearic acid.

A stainless steel pipe was cut into pieces of 10 mm × 10 mm and used as a substrate. The substrate was cleaned under ultrasonic agitation with acetone, ethanol, and distilled water at room temperature for 15 min, and dried by an N₂ blow. The substrate was textured by etching in hydrofluoric acid (HF) 50% for 5 – 30 min at room temperature, and then immediately soaked in distilled water at room temperature for 15 min and dried naturally in air. Zinc oxide seed was deposited on etched stainless steel substrate by using dip coating method. Precursor ZnO sol was prepared from 0.2 M zinc acetate in ethylene glycol. Dropwise of 0.24 M diethanolamine was added to the sol under continuous stirring at 60 °C for 60 min. The sol was aged for 24 h prior the seed deposition. Dipping and withdrawal speed of the substrate was set at rates of 5 cm/min, followed by drying in oven at 135 °C for 30 min. This seeding process was repeated thrice, and then the sample was heat treated at 300 °C for 60 min to crystallize the seeds.

ZnO nanorods were deposited on ZnO seeded stainless steel substrate by using chemical bath deposition (CBD) method. The precursor solution containing hexamethylenetetramine was prepared for various concentration zinc nitrate (5 – 35 mM) in ethanol-distilled water with volume ratio HMT:zinc nitrate of 1:3. The ZnO seeded stainless steel substrate was immersed vertically in the precursor solution at 80 °C for 6 h. After immersion, the ZnO coated substrate was rinsed with ethanol and distilled water, dried naturally in air, and then annealed at 400 °C for 60 min. To produce hydrophobic surface the ZnO coated substrate was immersed in stearic acid at various molarities (5-35 mM) and time (6-36 h).
2.3 Characterizations

Crystalline structure and surface morphology of the ZnO deposit was observed by X-Ray diffractometer (Philips PW-1830) using Cu Kα radiation (λ = 1.5405 Å). The surface microstructure of the samples was obtained with a scanning electron microscope (JEOL-JSM-6510LV), provided with energy dispersive X-ray (EDX) spectroscopy (JSM-6510LA). Water droplets of 5 μL on samples were captured by an optical charge-couple device (CCD, CNB-GP300CGG1), and the contact angle was analyzed by using ImageJ plug-in DropSnake [24]. Meanwhile, the reported values of contact angle were the average values of measured contact angle at four different locations of the sample surface. Sliding angle was obtained by measuring the tilted angle of the sample holder against the bench surface when the water droplet started to move. The composition of stearic acid and stearic acid modified ZnO nanorod was measured by Fourier transform infrared spectrometer (Shimadzu Prestige 21). All measurements were conducted at room temperature.

3. Results and Discussion

3.1 Surface structure of the substrate and ZnO coating

Figure 2 shows the surface morphology and contact angle of stainless steel substrate before and after etching in an HF solution. The surface morphology of the barestainless steel substrate has smooth texture in micron scales (Fig. 2a). EDX analysis showed that this bare substrate surface contained Fe, Cr and Ni elements with the atomic percentages of 69.9%, 16.6%, and 9.6%, respectively. This substrate surface has hydrophilic properties with a contact angle of 69.3°, which is typical of chemically untreated SS substrate [25]. Etching the substrate with hydrofluoric acid 50% for 5 min produced a porous surface with an irregular rough surface structure (Fig. 2b). The surface analysis of etched stainless steel indicated that the atomic percentages of Fe, Cr, and Ni on the surface decreased to 67.3%, 16.2%, and 9.6%, respectively, whereas O (oxygen) increased from 2.4% to 25.4%. The decrease of elemental metal and increase of oxygen were due to the formation of their oxides. Using XPS scanner, Lie et al. detected that the etched surface of the 304 stainless steel contains Fe₂O₃, FeF₃, Cr₂O₃, and CrF₂ on the surface of stainless steel substrate [26]. Naturally, oxide surface has hydrophilic properties. However, rough surface oxide provided air trapping underneath water droplets and increased the water droplet contact angle. As the etching time increased, the surface became rougher and reduced the contact angle (Fig. 2c). The decrease in contact angle is attributed to the high surface roughness in which the surface is physically unable to trap the water droplet anymore.
Fig. 2: SEM images of stainless steel substrates surface (a) before and (b) after after 5 min etching in 50% HF, and (c) contact angle of etched stainless steel substrates surface

Fig. 3: XRD patterns of ZnO on stainless steel substrate

Figure 3 shows the typical X-ray diffraction (XRD) pattern of ZnO deposited on etched stainless steel substrates. XRD pattern of stainless steel substrate is included to index the diffraction peaks of deposited ZnO. It is clearly shown that diffraction patterns of the deposited ZnO on ZnO seeds etched stainless steel substrate attributed to ZnO polycrystalline, and
corresponding a wurzite hexagonal ZnO (JCPDS No. 36-1451). No other peaks corresponding to impurity from zinc precursors was observed, confirming the pureness of the deposited ZnO. Evidently, the relative intensity ratio between (002) and (101) diffraction peak is quiet large indicating that the (002) peak is the preferential orientation in the c-axis alignment [27]. These results implied that ZnO seed on the substrate acted as nucleation center and provided preferred orientation for ZnO growth [28].

3.2 Surface morphology and wettability

Figure 4a-c shows top-view of SEM images of ZnO nanorods deposited on ZnO seeded stainless steel substrate for different ZnO precursor concentrations, under deposition temperature of 80°C for 6 h, immersed in 5 mM stearic acid for 6 h. It can be seen from Figure 4a that the ZnO nanorods grown with 5 mM precursor concentration have random direction staggered over the entire substrate surface. The implication is that the ZnO nanorods have a hexagonal shaped crystal structure with c-axis crystal orientation. ZnO nanorods at their final diameter and length were approximately 47-75 nm and 200-500 nm, respectively. However, as shown in Figure 4a, small portions of the substrate surface at different locations remained exposed. This exposure indicates that the deposition conditions with such low precursor concentrations at relatively low temperature (<90°C) was insufficient to provide the necessary amount of active precursors (Zn\(^{2+}\) ions) for growing the ZnO nanorods at all nucleation sites. On the other hand, for higher deposition temperature, i.e. 110°C or higher, Lee at al. succeeded in growing a relatively dense ZnO nanorods on ZnO seeded silicon substrate even when using very low (1 mM) precursor concentrations [29]. These results demonstrated that deposition temperature plays an important role in preparing active deposition precursors whilst the ZnO seed provides nucleation center for growing ZnO nanorods. When the ZnO precursor concentration was increased to 15 mM, denser ZnO nanorods were produced and fully covered the substrate surface in random directions. Increasing the concentration of ZnO precursor supplied larger amount of Zn\(^{2+}\) ions to produce denser ZnO nanorods. As seen in Figure 4b, the diameter and length of ZnO nanorods was about 72-98 nm and 500 nm, respectively. Further increasing the concentration of ZnO precursor to 35 mM resulted in much denser but irregular shapes and sizes of ZnO nanorods (Fig. 4c). Higher ZnO precursor concentration meant more Zn\(^{2+}\) available in the growth solution, and with availability of sufficient amount of HMTA to supply NH\(_3\) and OH\(^-\) through hydrolysis the growth rate of ZnO nanorods increased significantly [30]. There is a competition growth on all available nucleation sites on the substrate surface, as consequence of surface roughness and surface heterogeneity which provides more defects, steps, kinks, and vacancies. In addition, visual comparison of surface roughness of ZnO nanorods portrayed in Figure 4 clearly shows that ZnO nanorod surface produced by higher concentration of ZnO precursor seems to have smaller and more even surface roughness compared to that produced by smaller ZnO concentration, which may provide better air entrapment underneath the water droplet. It is also important to note that all ZnO nanorods deposited on ZnO seeded stainless steel always produces vertically unaligned ZnO nanorods. The explanation of underlying unaligned ZnO nanorods growth can be attributed mainly due to vertically unaligned orientation of ZnO seed deposited on rough stainless steel surface [31]. The proposed model for deposition of ZnO on ZnO seeded stainless steel is presented in Figure 4d.

The effect of concentration of zinc nitrate precursors and molarity of stearic acid on water droplet contact angle was shown in Figure 5. As shown in Figure 5a, the contact angle increases
almost linearly with the increase of the concentration of zinc nitrate. In correlation to deposited morphology shown in Figure 4, the more diluted zinc nitrate solution used in CBD, the denser ZnO nanorods was produced. Higher density of ZnO nanorods highlight the possibility that nanoscopic surface roughness not only improved the conformal coverage of stearic acid on nanorods, but also enhanced the surface sites for attaching stearic acid. Both effects simultaneously enhanced hydrophobicity of water droplet. Increasing the molarity of stearic acid from 5 mM to 8 mM improved the water droplet contact angle to no more than 10%, and only produced a maximum contact angle of 145˚C. However, increasing the molarity of stearic acid by more than 8 mM decreased the water droplet contact angle, as shown in Figure 5b. This suggests that 8 mM stearic acid provides full coverage of ZnO surface without modifying the surface morphology. Therefore, it seems that increasing the contact angle with stearic acid concentration is due to improvements in the coverage of stearic acid on the ZnO surface. It is commonly known that ZnO deposited by wet chemical contains –OH attached on ZnO surface has hydrophilic properties. Stearic acid molecules on ZnO surface are readily attached to these active –OH through on ZnO surface captured by the carboxyl group of stearic acid leading to lower surface energy. Increasing the concentrations of stearic acid supplied excess of carboxyl group of stearic acid on ZnO surface, which modified both the surface free energy and surface roughness. Excess stearic acid on the ZnO surface reduces the surface roughness and may provide extra hydrophilic stearic acid head, which in turn reduces the water droplet contact angle [32].

Fig. 4: SEM images of ZnO nanorods on ZnO seeded stainless steel deposited with concentration of zinc-nitrate of (a) 5 mM, (b) 15 mM, and (c) 35 mM, immersed in 5 mM stearic acid for 6 h, and (d) schematic representation of ZnO nanorods growth. Insets show the images of the water droplet on the ZnO/SA surface.
The variation of immersion time in stearic acid (8 mM) for a sample deposited with 35 mM zinc nitrate affects the hydrophobicity, as shown in Figure 6 (including the corresponding images of water droplets on ZnO nanorods coated stainless steel). Figure 6a clearly shows that the contact angle increases with immersion time, with the maximum contact angle of 162° obtained at 36 h of immersion. It seems that the carboxyl group of stearic acid rearranges themselves to attach the active –OH on the ZnO nanorod surface, which occurs in a very slow process, and the immersion time of 36 h may not be the final stage in formation of a monolayer stearic acid on ZnO nanorod surface. A full coverage a monolayer stearic acid on ZnO nanorod surface is one requirement for producing maximum water repellent. Spalenka et al. required about 2 h immersion to cover a monolayer stearic acid molecule on a spin coating of ZnO/SiO₂. The use of tetrahydrofuran as a solvent, which has a smaller dissociation constant for carboxylic acid, slows down the acid part of stearic acid to directly attack the ZnO surface and allows stearic acid to react with the ZnO surface. On the other hand, using stearic acid in ethanol with the same concentration completely dissolves the ZnO thin film within 72 h [33]. In this study, ethanol was used as a solvent for preparing 10 mM stearic acid solution. Ethanol dissociated hydrogen ion in stearic acid five orders of magnitude higher than tetrahydrofuran, implying that etching ZnO has taken place during immersion the sample in stearic acid solution. During functionalization, the ZnO surface in stearic acid entered dynamic competition between etching ZnO surface by acid and depositing stearic acid on ZnO surface. The balance reactions may slow down the attachment process of stearic acid to the active hydroxyl on ZnO surface. Immersing the sample in stearic acid ethanol solution of 10 mM for 36 h may not be sufficient to fully cover ZnO surface with stearic acid. For comparison, to produce a SAM of full coverage adsorption of stearic acid on sapphire requires 165.5 h using 1.5 mM stearic acid n-hexadecane solution at room temperature [34].
Thus, the movement of water droplet on ZnO nanorod surface was determined by the friction force of ZnO surface against water droplet movement, which largely depends on sliding angle and weight of water droplet. The sliding angle is affected by the mass of the water droplet and gravitational force. Gravitational force promotes the water droplet to move effortlessly on the ZnO nanorod surface. As the friction force of the ZnO nanorod surface becomes smaller, the water droplet easily moves. Guo et al. formulated the maximum friction force as $f_{\text{max}} = mg \sin \theta$, in which $f_{\text{max}}$ is the maximum friction force, $m$ is the mass of water droplet and $g$ is the earth gravitational constant [35]. Using the aforementioned equation, the friction force of 5 μL water droplet on ZnO nanorod surface treated with 8 mM stearic acid at different immersion time can be calculated. The maximum friction force of ZnO nanorod surface immersed 6 h in stearic acid which allows the water droplet begin to move is calculated to be 10.66 μN, at sample tilting angle of 12.6°. The friction force value drops significantly to 3.24 μN when the ZnO nanorod surface is treated in stearic acid for 36 h, corresponding to the sliding angle of 3.8°.

### 3.3 Surface composition of ZnO nanorods treated by stearic acid

ZnO coated stainless steel surface covered with hydroxyl groups in water is a hydrophilic property. When the active –OH on ZnO surface is in contact with carboxyl group of stearic acid during the immersion of the stearic acid, heads of hydroxyl groups react with hydroxyl groups and release water, which modifies the ZnO surface into the hydrophobic state. To understand the surface modification of ZnO nanorods with stearic acid, Fourier transform infrared spectroscopy was carried out to obtain infrared transmittance spectra of pure stearic acid and stearic acid modified ZnO surface. Comparison of those spectra provides signature of bonding interaction between carboxylate head of stearic acid, i.e. -OH (C-O-H), C-O and C=O, with hydroxyl on the ZnO nanorod surface.
Figure 7a shows FTIR spectrum of pure stearic acid prior absorbing onto ZnO surface, with featuring group of infrared absorption peaks at frequency region of the C-H stretching vibration (3000-2800 cm\(^{-1}\)), the C-O stretching vibration (1800-1350 cm\(^{-1}\)), and the O-H bending and swinging vibrations (1100-600 cm\(^{-1}\)) [36]. Two peaks at 2916 cm\(^{-1}\) and 2849 cm\(^{-1}\) corresponded to asymmetric and symmetric CH\(_2\) vibrations, respectively, of long chain stearic acid. The peak at 2957 cm\(^{-1}\) and small shoulder peak at 2890 cm\(^{-1}\) are attributed to asymmetric and symmetric CH\(_3\) vibrations, respectively [37]. The absorbance intensity of CH\(_2\) is larger than that of CH\(_3\) because of the long hydrocarbon chain of stearic acid. Two peaks at 1705 cm\(^{-1}\) and 1467 cm\(^{-1}\) indicate the vibration mode of C=O and C-O, respectively [38]. Peaks 1431 cm\(^{-1}\) and 1410 cm\(^{-1}\) are assigned to group vibration of C-O-H [38]. The vibration band between 1300 and 1400 cm\(^{-1}\) contains a wagging vibration of CH\(_2\) group at 1350 cm\(^{-1}\) for double gauche defect [39], and peaks at 943 cm\(^{-1}\) and 723 cm\(^{-1}\) attributed to the out-of-plane bending and the in-plane swinging vibration of -OH, respectively [35]. Peaks at 1016 cm\(^{-1}\), 810-762 cm\(^{-1}\) and 890 cm\(^{-1}\) represented CH\(_2\) and CH\(_3\) rocking modes, and peak at 686 cm\(^{-1}\) attributed to O=C=O in plane angle deformation [40].

After stearic acid modification of ZnO nanorod surface, the infrared spectra (Fig. 7b) depicts that the asymmetric and symmetric CH\(_2\) and CH\(_3\) vibrations are remain observable, but they shifts to the higher frequencies. This process suggests that the stearic chains are attached to the ZnO surface in random orientations on ZnO nanorod surface. The peak of symmetric CH\(_3\) vibrations is hardly discernible. The peak intensities of the CH\(_2\) vibrations is much larger compared to those of the CH\(_3\) vibrations, implying that the long hydrocarbon chain of stearic acid is slightly tilts away from the ZnO surface normal [41,42]. The vibration peak of C=O remained present in the spectra but shifted and split into three peaks of C=O vibrations at 1743 cm\(^{-1}\), 1696 cm\(^{-1}\) and 1650 cm\(^{-1}\). The carboxyl group vibrations at 1743 cm\(^{-1}\) is configerative of a unidentate bonding of stearic acid to ZnO surface. The peaks at 1696 cm\(^{-1}\) and 1650 cm\(^{-1}\) are asymmetric C=O stretching with double bonds attached to the surface as a bidentate modes. The C-O stretching group vibration at 1467 cm\(^{-1}\), 1431 cm\(^{-1}\) and 1410 cm\(^{-1}\) as well as the group vibration of –OH peaks at 943 cm\(^{-1}\) and 743 cm\(^{-1}\) disappear, suggesting that the reaction head of stearic acid with –OH on the ZnO surface has taken place. New peaks that appeared at 1524
cm$^{-1}$ and 1461 cm$^{-1}$ are considered stearate characteristic absorption with a symmetric (bidentate bridging) bonding mode of carboxylate [34]. The wagging vibration of CH$_2$ group remained present in the stearic acid treated ZnO infrared spectra that vibrated at a slightly higher frequency, meaning that the chemical state of CH$_2$ wagging group was not altered during the chemisorption process. The infrared vibration spectra between 1050 cm$^{-1}$ and 600 cm$^{-1}$ have no peak, indicating that the –OH bending and swinging vibrations of stearic acid has completely reacted with hidroxyls on ZnO nanorod surface.

4. Conclusions

ZnO nanorods coated in stainless steel were successfully prepared by chemical bath deposition of ZnO seeded 316 stainless steel substrate. ZnO seed facilitated the formation of nanorod structures, and variation of precursor concentrations provided means to control the surface coverage and thin film conformity. Higher concentration of zinc-nitrate precursor produced denser ZnO nanorods. Growth of denser ZnO nanorods on unaligned orientation of ZnO seed results in the desired surface roughness structure required for the formation of superhydrophobic surfaces. Tuning the concentration of stearic acid and immersion time for a sample plays an important role in creating the low surface energy of ZnO nanorods.

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6. References

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