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Superhydrophobic and Highly Oleophobic Zinc Sheet Surfaces Developed by a Simple Technique

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Abstract: In this report, superhydrophobic and highly oleophobicmicro- nano-scale roughened Zn sheet surfaces were obtained. A simple and environmentally friendly technique of immersing Zn sheets in hot deionized water was used to grow ZnO nanorods. Variation of the immersion time had a significant impact on the evolution and formation of the nanorods. After their concealing with long chain fluorocarbon oligomers of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTS), ZnO nanorod surfaces prepared at 60 min immersion time showed the highest wetting repellency properties toward water and peanut oil. However the surfaces yet to be able to super repel the two liquids. In order to improve the Zn sheet surfaces repellency toward liquids with various surface tensions, hierarchical structures with the combination of both micro channels covered-up with ZnO nanorods were developed. Simple technique of one-directional mechanical sanding was used to impart micro channeled structures onto Zn sheet surfaces and post immersion in hot de-ionized water for ZnO nanorods cover-up. The concealed micro-nano- combination structures with 1H, PFDTS oligomers showed superhydrophobic and highly oleophobic properties. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Photoluminescence (PL) techniques were used to characterize the morphology of the prepared surfaces.

Key words: Zn sheet, hot water, ZnO nanorods, hierarchical structures, superhydrophobic, oleophobic.

1. Introduction

In terms of structural properties, ZnO material can be formed in a wide range of morphological structures such as nanorods, nanowires, nanorings, nanobows, nanobelts, nanocomb, nanoflowers and nanopropeller [1]. This diversity in nanoscale morphological structure of ZnO has made it as a potential candidate for many technological applications. In addition to its wide potential application in electronics, it can also be used for the manipulation of solid surfaces wetting properties due to both significant increase in the surface area-to-volume ratio as well as transparency property of the material [2, 3]. Solid surfaces with customized wetting properties could be used for a variety of applications such as self-cleaning, anti-fouling, anti-drag, water condensation, and water/oil separation. In addition, the efficiency of devices with such surface-wetting customized properties toward liquids is enhanced according to the existing environmental conditions.

Wetting properties of “smooth” solid surfaces is characterized primarily by the liquid droplet’s contact angle, according to Young’s model, while rested on the surface [4]. Contact angle of a liquid droplet is the angle between a tangent line to the droplet’s side and the droplet’s baseline. Its range is between 0°-180° depending on both solid surface’s physical and chemical properties. A solid surface demonstrating a contact angle in the range of 10°-90° is known as a hydrophilic surface when the probe liquid is water and an oleophilic surface when the probe liquid is an organic liquid such as oil. In other words, the solid surface has the tendency toward wetting. For solid surfaces with a liquid contact angle in the range of 90°-150° are known as hydrophobic surfaces for water and oleophobic surfaces for organic liquids, demonstrating anti-wetting tendency. Solid surfaces with extreme liquid contact angles ranging from 0° to

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10° are known as superhydrophilic (for water) and superoelophilic (for organic liquids), while the one with liquid contact angles ranging from 150° to 180° are known as superhydrophilic (for water) and superoelophilic (for organic liquids). Solid surfaces with both superhydrophobic and superoelophobic property are known as superamphiphobic surfaces that are useful for self-cleaning, anti-icing, anti-fouling and anti-drag applications [5].

Wetting properties of a solid surface can be manipulated by introducing physical and/or chemical modifications to the surface. Roughening magnifies wetting properties by the degree of increase in the actual surface area compared to the corresponding apparent area [6, 7]. In terms of chemical modifications, lowering the surface energy of a solid surface reduces its tendency to interact with liquids and consequent rise in the liquid droplet’s contact angle. Nevertheless, the liquid’s surface tension is also another vital parameter in determining the interaction mechanism between liquids and solid surfaces. Liquids with lower surface tensions such as organic liquids tend to interact more vigorously with solid surfaces, promoting lower contact angles. Therefore, developing rough solid surfaces that can strongly repel organic liquids such as oils is more challenging. In spite of chemical modification of rough solid surfaces with the lowest surface energy materials such as long chain fluorocarbons oligomers, carefully engineered rough structures with re-entrant propertyor combination of specific micro- nano-structured surfaces are demanded in order for the solid surface to strongly repel oils [8-10].

There have been reports on developing superhydrophobic ZnO nanostructured surfaces for anti-wetting applications [2, 3, 11-17]. Kwak et al. [14] reported superhydrophobic ZnO nanorods grown by wet-chemical technique after their surface modification with long chain hydrocarbon oligomers. It was also shown that the repellence tendency of the developed ZnO nanorod surfaces enhanced with the increase in hydrocarbon oligomers chain length. In another study by Gong et al. robust superhydrophobic ZnO nanowires were obtained after being grown on silicon micro pyramids structures without any post surface chemistry modification. Increase in the length of ZnO nanowires contributed in water droplet’s transition from Wenzel state (wetting state) to Cassie state (non-wetting state). Wu et al. [2] also reported hybrid superhydrophobic ZnO surfaces grown by hydrothermal technique. The combination of ZnO nanorods topped with a porous zinc layer showed higher degree of stability.

Various techniques have been used to grow micro and/or nanostructured ZnO surfaces according to the suitability of ZnO developed nanostructures for a particular application [18-26]. The techniques used to grow ZnO nanostructures based on the required growth temperature and complexity can be divided into three main categories: First, high-temperature (> 500 °C) thermal evaporation techniques such as metal-organic chemical vapor deposition, solid-vapor deposition, vapor-liquid-solid growth, and high pressure pulsed laser deposition. Second, moderate-temperature (> 100-500 °C) mechanisms such as: wet oxidation, glancing angle deposition. The third category is low temperature (< 100 °C), simple-solution based techniques such as; hydrothermal, sol-gel, electrochemical deposition, and wet-grinding. A specific growth technique can be used based on the demand for Zn oxide materials with a particular morphology and the choice of a substrate.

In an attempt to produce higher quality ZnO nanostructures using low temperature and simple-solution based techniques, Tan et al. [24] treated Zn foil with hot de-ionized water at 90 °C for relatively long periods of time ranging from 4 to 24 h, in their study 2D nanosheets with different morphologies were obtained. In another study by the same group, ZnO nanowires were obtained after the polished Zn-foils pre-etched and then treated in hot de-ionized water for the same time periods. In both studies crystalline ZnO nanosheets and nanowire structures were reported.

In this study and encouraged by our previous studies on the treatment of metallic surfaces with hot de-ionized water for developing nanostructured metal oxide surfaces for anti-wetting property [27-29], the treatment of Zn sheet surfaces with hot water was carried out. Using this simple and environmentally friendly technique for relatively short durations ranging from 1 to 120 min, crystalized ZnO nanorods with different shapes and morphological structures were imparted onto Zn sheet surfaces. In addition, hierarchical structures with the combination of micro channels covered-up with ZnO nanorods were also grown. Simple one-dimensional mechanical sanding was used to impart the micro channels onto the Zn sheet surfaces. The developed Zn sheet surfaces of micro, nano, and micro + nano were concealed with long chain fluorocarbon oligomers for anti-wetting property. The wetting characterization of the prepared Zn sheet surfaces was performed by using both water and peanut oil liquids. The morphology and the structure of the prepared surfaces were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and Photoluminescence (PL) techniques.

2. Materials and Method

2.1 Surface Roughening

First, commercially available Zn sheets with 1.0 mm thickness were cut into substrates with dimensions of (2.5 cm X 2.5 cm). For the removal of both the native oxide layer and environmental contamination, the substrates were polished using mechanical sanding utilizing two different ultrafine sandpapers of 2500 and 3000 grits, respectively. The flat-polished substrates were ultra-sonicated in acetone for 5 min and rinsed with de-ionized water. Next, the cleaned flat-polished zinc substrates were immediately immersed in hotde-ionized water (~100 ^{o}C) for the various durations of 1, 5, 20, 60 and 120 min. Hierarchical micro- nano-structured Zn sheet surfaces were obtained by first mechanically sanding the surfaces with 400 grit sandpaper for only 20 seconds. The sanding was carried out in one direction in order to impart micro channels to the Zn sheet surface. After cleaning, the developed Zn sheet surfaces with micro-channels were immersed in hot de-ionized water (~100 °C) for a duration of 60 min to be covered-up with ZnO nanorods.

2.2 Surface Characterization

Morphology and geometrical dimensions of the formed micro-channels and ZnO nanorods were analyzed by top-view and cross-sectional scanning electron microscopy (SEM, JEOL 7000F) imaging. The crystal structure and orientation of the ZnO nanords were analyzed using X-ray diffraction (XRD, Bruker D8-Discover). Room temperature photoluminescence (PL) spectra of the ZnO nanostructured surfaces were obtained by using the He-Cd laser (IK Kimmon laser, IK5652R-G) with a wavelength of 325 nm and max power of 200 m was the excitation light source. After an exposure time of 15 s, PL emission from the samples was collected by a detector (HORIBA JOBIN YVON, iHR320) with a vertical slit width of 0.4 mm. PL measurements covered a spectral range from 150 to 1,230 nm.

2.3 Surface Chemistry Modification

The roughened Zn sheet surfaces were immersed in hexane solution of 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDTS) oligomers for 60 minutes. The chemically modified samples were rinsed with de-ionized water and placed inside oven under 90 °C for another 60 min in order for the reaction to be completed as well as removal of the unattached PFDTS oligomers. Finally, the surfaces were left in an ambient environment overnight.

2.4 Wetting Analyses

Wetting analyses of the physically and chemically modified Zn sheet surfaces was carried out using a

VCA Optima goniometer. Liquid droplets of 5 ± 1 μl size of both water and peanut oil were gently dispensed on the surfaces. The Sessile Drop method was used to measure the CAs of the captured digital images.

3. Results and Discussion

Fig. 2 shows the top- and tilted-view SEM images of Zn sheet surfaces immersed in hot de-ionized water for durations of 1, 5, 20, 60 and 120 min. A significant evolution in the morphology of nanostructures as the function of treatment time can be noticed. For the first min of immersion of Zn sheet substrates, individually separated tiny nanorods with an average size of less 20 nm are formed on the surface. After 5 min of immersion, densely packed and larger nanorods with a clear vertical preferential growth are developed. With the progress of the immersion time to reach 20 min, dense and well vertically aligned individual nanorods are formed. According to the SEM images depicted in Fig. 2d, the ZnO nanorods possess two distinct diameters of around 20 and 50 nm both with a vertical height of slightly more than 100 nm. After 60 min of immersion, nanorods with diameters of 50-75 nm and vertical heights of around 250 nm were formed which is twice the size of the nanorods formed after 20 min of immersion, Fig. 2e. Interestingly, the increase in immersion time of Zn sheet in hot water from 60 to 120 min showed decrease in the lateral size of nanorods with no significant variation in their vertical height. This indicates that the relatively well-aligned, individual and mono-dimension nanorods are formed after 60 min of immersion in hot water. In the studies carried out by Tan and his group [24] in treating unetched and etched Zn foil with hot water (90 °C), ZnO nanowires with 750 nm length for the etched Zn

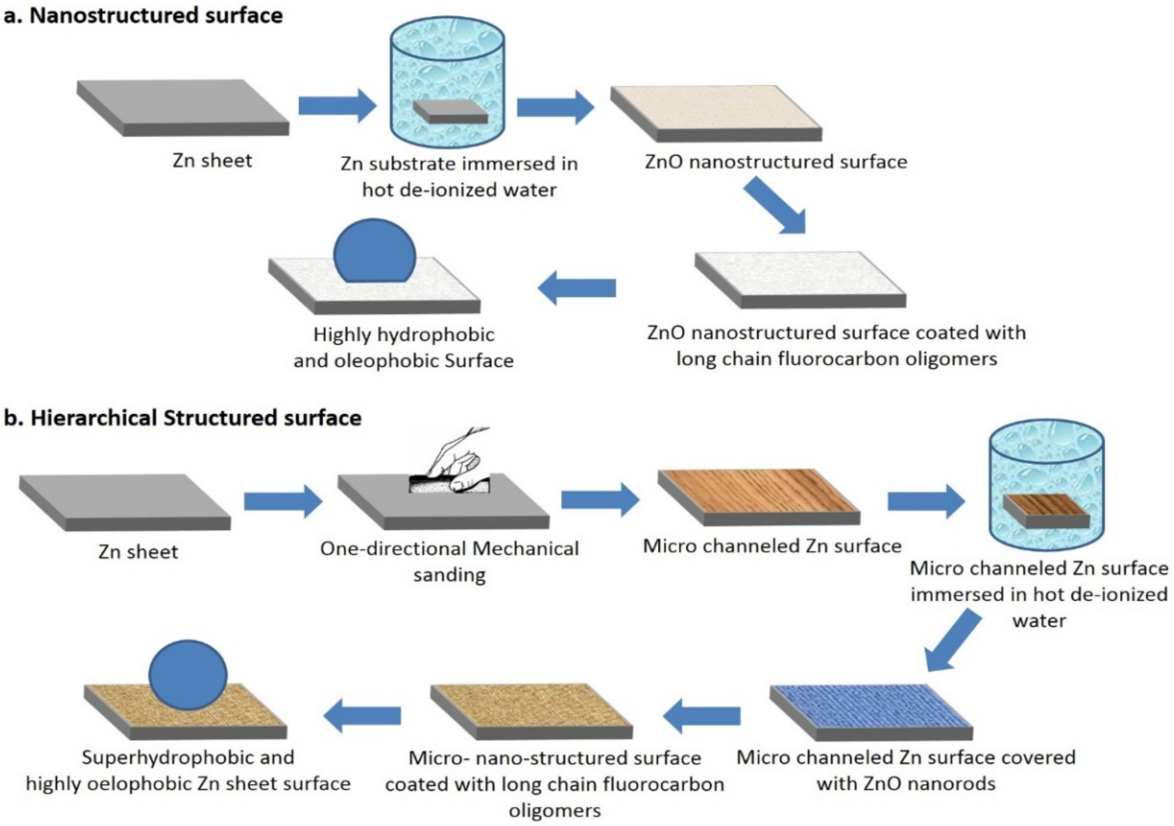

Fig. 1 Schematic representation of the experimental procedure (a) developing hydrophobic and oelophobic nanostructured Zn surface and (b) developing superhydrophobic and highly oleophobic hierarchical rough surface with micro channels covered with ZnO nanorods.

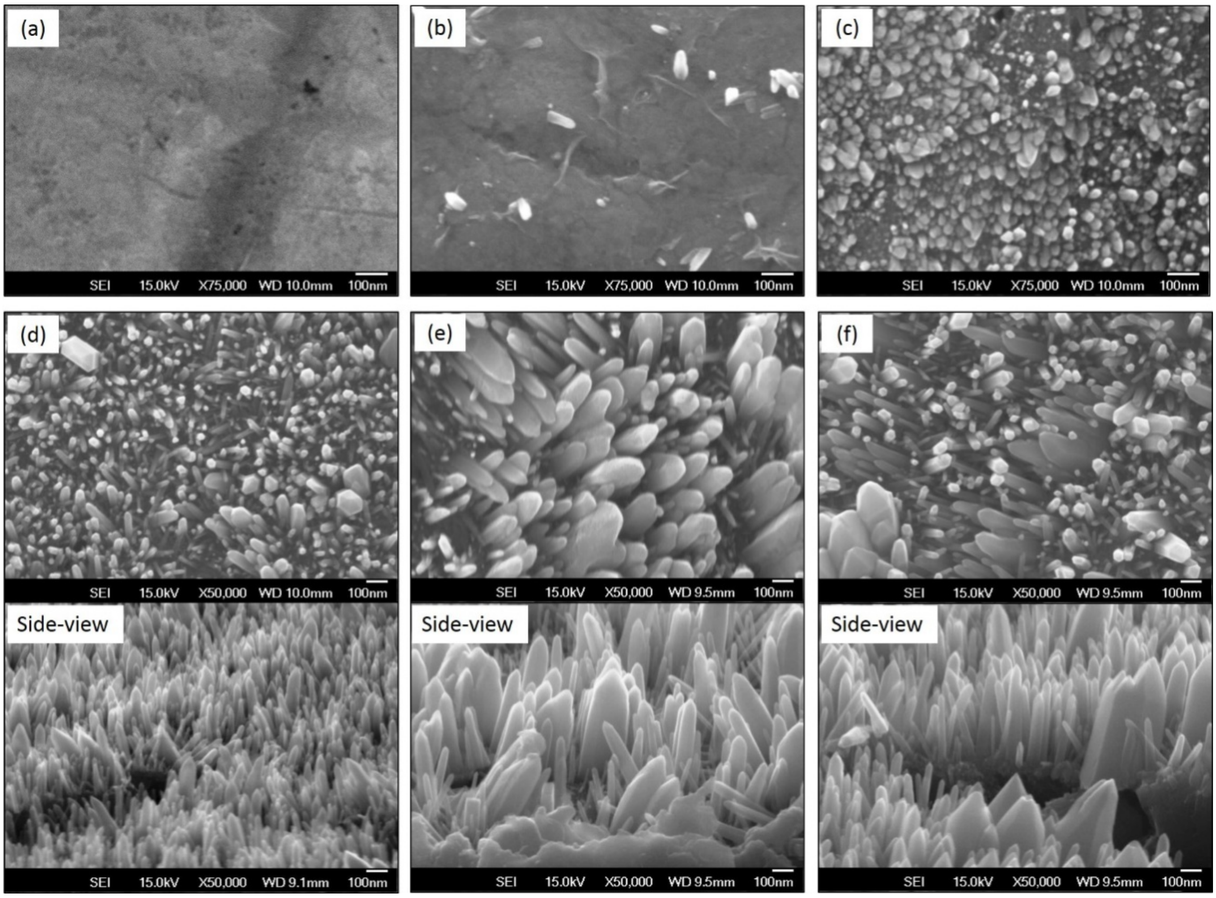

Fig. 2 SEM images of immersed zinc sheets in boiling DIW for various time periods of (a) untreated, (b) 1 min, (c) 5 min, (d) 20 min, (e) 60 min and (f) 120 min.

foil and dense nanosheets for the un-etched Zn foil were obtained.

The hexagonal shapes of the nanorods with multifacet tips is a primary manifestation of ZnO structures that have been widely reported in literature. To confirm that the obtained structures are ZnO with wurtezite structures, XRD analysis was carried out. The XRD peaks of the immersed Zn sheets in hot water for the different imerssion time periods are depicted in Fig. 3a. For the polished Zn sheet but untreated in hot water, peaks can be observed at 36.2°, 38.9°, 43.2° and 54.4° correspond to the (002), (100), (101) and (102) orientations, respectively. For the Zn sheets treated in hot water for various durations, due to the strong peaks coming out from the Zn substrate only small peaks can be located that correspond to ZnO crystal structures. In addition, both Zn and ZnO materials share the same peak at 36.2° but for the different orientations of (002) and (101), respectively [24, 30, 31]. With the progress in treatment time individual low intensity peaks from ZnO structures can be observed at different angles represnting the variation in the orientation of their crystal structure as the nanorods grow in size.

In order to be more certain that obtained nanorods are ZnO nanostructure and investigate their crystal quality and bandgap properties, room temperature PL analysis of the nanostructured surfaces was also performed. Fig. 3b shows the PL spectra of untreated Zn sheet and Zn sheet surfaces treated in hot de-ionized water for various time periods of 1, 5, 20, 60, and 120 min. In general, a main intense band of UV emission is observed at 377-391 nm, associated with the energy band gaps of 3.28-3.17 eV. The plot shows that the band intensifies with the increase in treatment time, which is consistent with the morphological

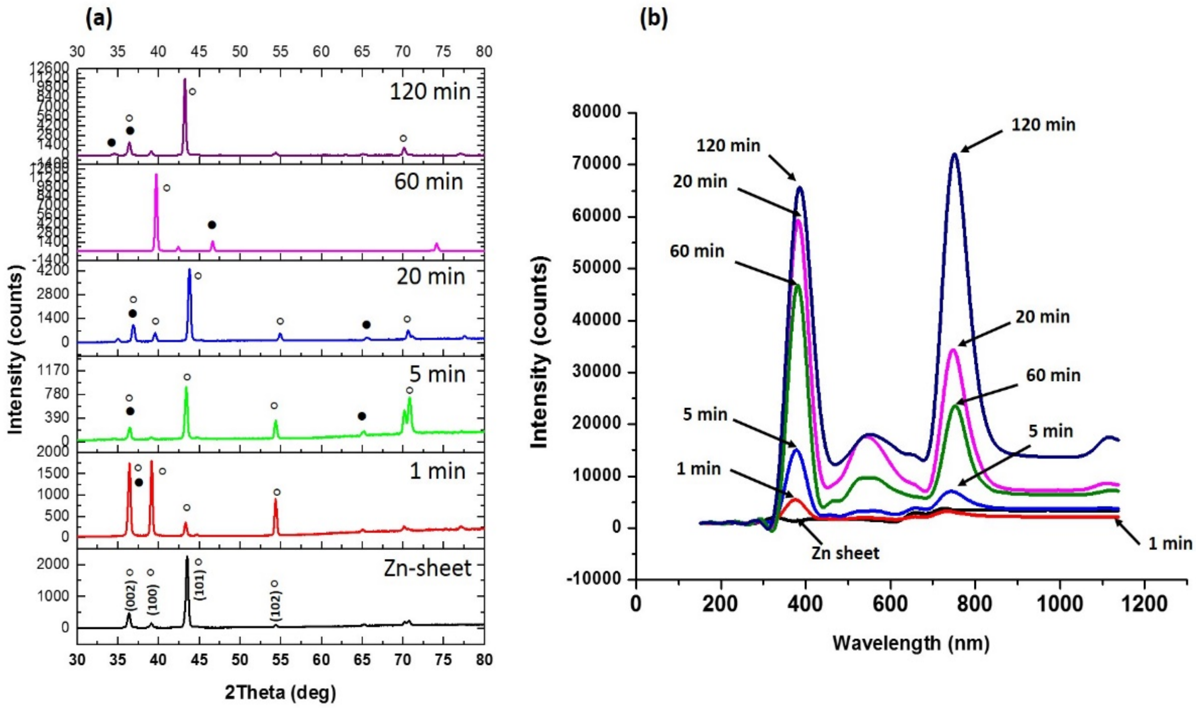

Fig. 3 XRD and photoluminscence spectra of the untreated and treated Zn sheet srfaces in hot de-ionized water for different time periods of 1, 5, 20, 60 and 120 min.

growth of ZnO nanostructures. However, ZnO nanorods obtained after 20 min of immersion showed more intense peak compared to the ZnO obtained after 60 min of immersion, which indicates higher quality ZnO nanorods after 20 min immersion compared to the one obtained after 60 min immersion. The energy band gap of the obtained ZnO nanorods is relatively consistent with the reported energy band gaps of ZnO nanorod and nanowire structures. The second intense band is observed at infrared region with a wavelength of ~743 nm, associated to narrow band gap of 1.66 eV. The third but weakest band is located in the green region at 545-521 nm associated to energy band gap of 2.27-2.38 eV. According to literature, the band observed in the green region is believed to be due to both defects in the structure of the obtained ZnO nanorods and/or size effects of the nanorods [31].

The formation mechanism of the ZnO nanorods formed on the surface of Zn sheets after their immersion in hot de-ionized water can be explained in the context of the both hydrothermal and wet oxidation techniques. In the hydrothermal technique double-positive Zn ions (Zn^{2+}) are generatedas the result of chemcial reactionsbetween the mixed solvents. With time progress and sustained heat (90 °C), $Zn(OH)_2$ moleculesare generated after Zn^{2+} ion hydrolyses combined with two negative hydroxyl groups ($2OH^-$). Finally and due to the saturation of the Zn sheet surfaces with $Zn(OH)_2$ molecules, ZnO structures began to nucleate as the intial stage of ZnO nanostructure’s growth. In our case of hot water treament, no chemical solvents are involved to obtain the Zn^{2+} ions, so we believe that the source of Zn^{2+} ions on the surface of Zn sheet is the diffusion of Zn atoms across the surface. This is similar to the case of wet oxidation of Zn films for developing ZnO nanostructures but under much higher temperature approaching Zn melting point (420 °C). Furthermore, the source of providng the OH^- groups could be the interaction between both Zn surfaces and H_2O molecules at which the surface of the Zn metallic sheet acts as a catalyst to break down water molecules into OH^- and H^+. Each of a two hydroxl groups ($2OH^-$) bonds into a diffused zinc ion (Zn^{2+}) and forms $Zn(OH)_2$ molecules. Next, nucleation of ZnO nanostructures starts to initiate due to the saturation of the surface with Zn^{2+} ions. The formed ZnO nucleation sites promote the formation of ZnO nanostructures by a sequence stacking of Zn^{2+} and O^{2-} to form nanorods. The folowing two equations showcase the formation process of ZnO nanorods [32, 33].

$$Zn^{2+} + 2OH^{-} \leftrightarrow Zn(OH)_2 \tag{1}$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \tag{2}$$

In order to develop hierarchical structures with both micro- nano- combination, simple mechanical sanding technique was combined with hot water treatment technique. Fig. 4 shows the SEM images for the developed hierarchical structures of Zn micro channels uniformly roofed with ZnO nanorods. The micro channels were imparted via one-directional mechanical sanding using 400 grit and post immersion in hot water for the duration of 60 min. As shown in the SEM images, the channels have dimensions with few microns and a relatively unequal distance from each other ranging from few microns to more than 10 microns. For more uniform micro channels in terms of dimensions and separation distance, a more sophisticated mechanism for mechanical sanding is required. In spite of that, the channels are uniformely roofed with ZnO nanorods with dimensions and shapes close to the ones obtained on smooth Zn sheet shown in Fig. 2e. Interestingly, the inner sides of micro channels are also uniformly concealed with ZnO nanorods, as demonstrated in the magnified SEM images of Fig. 4, which could enhance the re-entrant property of the hierarchical structures. In addition to both roughness and low surface energy, the property is required for the engineered surfaces to strongly repel low surface tension liquids.

In order to impart liquid repellency property toward water and oils onto the prepared Zn sheet surfaces of nanostructures, the surfaces were concealed with long chain fluorocarbon oligomers of PFDTS. Wetting

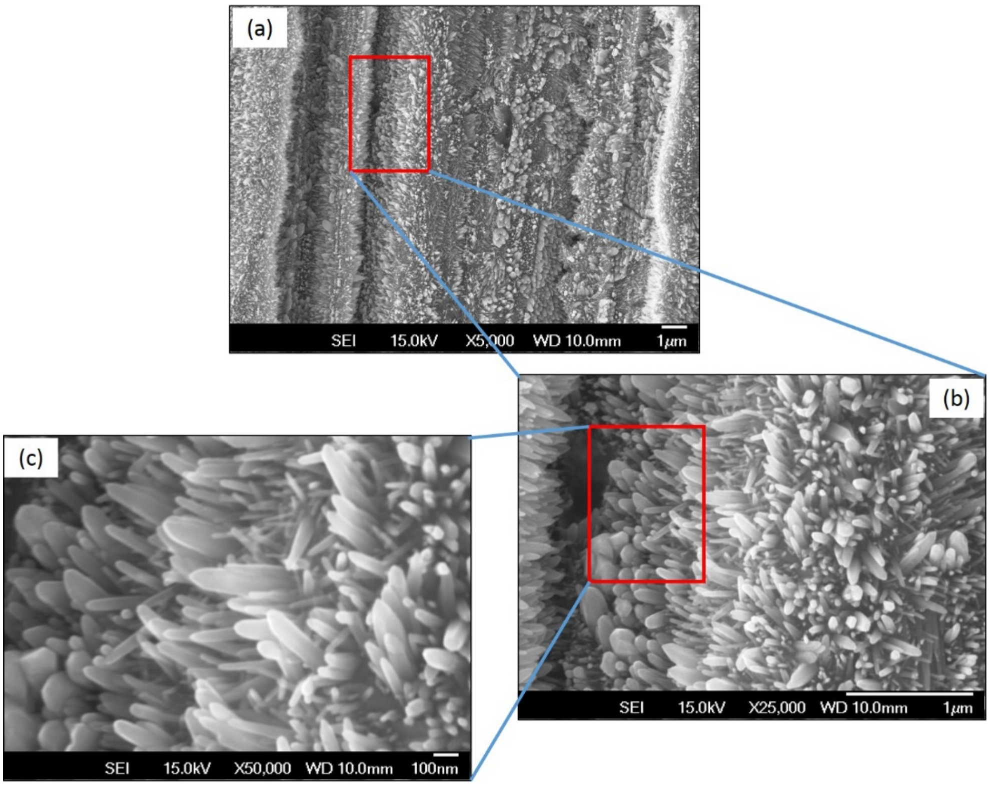

Fig. 4 SEM images of Zn micro channels covered with ZnO nanorods obtained by combination of both mechanical sanding with 400 grit sandpaper and post treatement in hot water for 60 min.

characterization of the Zn sheet surfaces with ZnO nanorod structures after being concealed with PFDTS oligomers is depicted in Fig. 5. A clear trend of increase in the values of both water and peanut oil contact angles is observed with the increase in the immersion time of the surfaces in hot water for the first 60 min time period. However, for the surfaces treated for 120 min duration, lower contact angles for both liquids were observed compared to the 60 min immersion time. This can be qualitatively attributed to the fact that ZnO nanorods obtained for 60 min immersion time, as shown in the SEM images of Fig. 2e, are better individually-aligned with larger lateral and vertical dimensions. All these parameters promote significant increase in the apparent surface area of the obtained rough surfaces which in turns magnifies the liquid repellency of the surfaces. The surface observed a water contact angle of 141° and a peanut oil contact angle of 100°, see Fig. 5b. The wetting repellency property of the prepared surfaces is significantly enhanced, but hasn’t reached super repellency at least toward high surface tension water.

In order to enhance the wetting repellency of the Zn sheet surfaces toward liquids to reach super-repellency, a combination of Zn micro channels covered-up with ZnO nanorods were also developed. The wetting properties of the hierarchical structured Zn sheet surfaces after being concealed with long chain fluorocarbon oligomers of PFDTS were also measured. The micro channel structures covered-up with nanorods observed water contact angle of 157° and peanut oil contact angle of 118° as shown in the Fig. 6. The figure also illustrates the effect of different ugh scales of micro, nano and the combination of micro/nanostructures imparted onto Zn sheet surfaces, after being concealed with long chain fluorocarbon oligomers of PFDTS, on their wetting repellency properties. In terms of high surface tension water, the wetting repellency of the prepared Zn sheet surfaces monotonically increased starting from contact angle of 127° for micro-rough structures, 141° for nano-rough structures, and reaching superhydrophobicity with contact angle of 157° for combined micro-nano rough structures. For the low surface tension liquid of peanut oil, the same trend of enhancement in the repellency properties of the prepared surfaces can be noticed but with relatively lower contact angles. It is concluded that the Hierarchical structure design significantly enhanced the repellency of the Zn sheet surfaces toward high surface tension liquids such as water and with a lower rate toward low surface tension liquids as well.

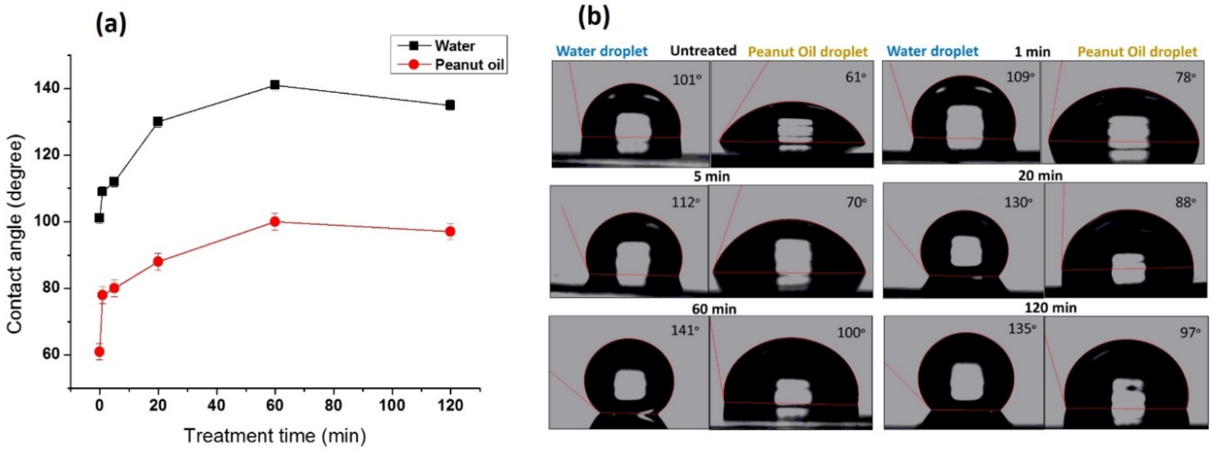

Fig. 5 (a) Water and Peanut oil contact angles versus treatment time of Zn sheet surfaces with hot de-ionized water (~100 °C) and post concealing with long chain fluorocarbon oligomers, (b) digital images of both water and peanut oil droplets.

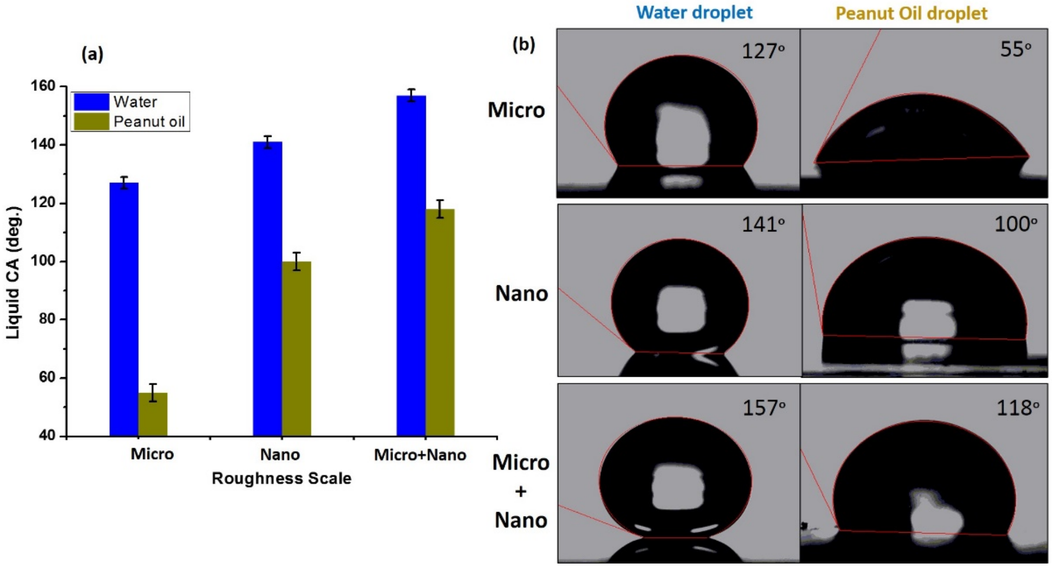

Fig. 6 (a) Water and Peanut oil CAs versus the three different roughness scales of the developed Zn sheet surfaces concealed with long chain fluorocarbon of PFDTS oligomers, (b) digital images of both water and peanut oil droplets while rested on those surfaces.

4. Conclusions

Simple and eco-friendly technique of mechanical sanding combined with hot water treatment is used to develop highly liquid repellent Zn sheet surfaces toward both high and low surface tension liquids after lowering their surface energy with long chain fluorocarbon oligomers. Nano-scalerough surfaces with various dimensions and density formed by hot water treatment significantly enhanced the Zn sheet surfaces liquid repellency properties. However, super repellent Zn sheet surfaces toward high surface tension liquids and high repellency toward organic liquids were only obtained after combining both mechanical sanding and hot water treatment for developed micro- nano-structured combination and its post concealing with long chain fluorocarbon oligomers.

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