

# Fabrication of Superhydrophobic Surface of ZnO Thin Films by Using Oleic Acid

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**Abstract:** Zinc oxide (ZnO) nanostructures were successfully prepared by a simple, highly efficient, and low-cost using the hydrothermal method. A superhydrophobic surface with a static water contact angle (CA)  $>150^\circ$  has been synthesized by modifying ZnO nanostructures with  $100^\circ\text{C}$  at 1 h stable oleic acid (OA) as coupling agents, in order to modify their surface properties and make them more hydrophobic. Surface modification of ZnO nanostructures has been performed, and the effect of the modification on the structure and morphological properties were investigated. The resulting nanostructures were characterized by XRD, FESEM, UV-VIS spectroscopy. XRD pattern revealed that ZnO nanostructures prepared by hydrothermal method (crystallite size  $\sim 30$  nm) have hexagonal wurtzite structure with a good crystalline quality. FESEM images of ZnO nanostructures prepared by hydrothermal showed hexagonal nanorods assembled in flower-like shape, there was much change in the surface morphology of modified samples after surface modification such as (nanorods, nanoflowers, and nanotube). Results show the water CA of ZnO superhydrophobic surfaces increased steadily from  $147\pm 2^\circ$  to  $154\pm 2^\circ$  when the OA weight percentage increased from 2mg to 10mg. The optical measurements for ZnO nanostructures showed that all samples the absorption band in the ultraviolet region. The band gap of pure ZnO nanostructures 3.5 eV and after modification ZnO surface 3.6 eV. All samples of ZnO were maintained at room temperature for 1 hour to 5 months to test the stability of the surface. The water CAs were measured for each condition, and very little change was observed in the CAs. In addition, the ZnO surface remained superhydrophobic without any contamination observed after water was sprayed on it.

**Keywords:** Superhydrophobic Surfaces, Zinc Oxide, Nanostructures, Oleic Acid, Surface Modification, Hydrothermal Method

## 1. Introduction

Wettability is a surface property, that plays a significant role in surface functionality such as fluid transport, vapor condensing, fouling resistance, and contamination removal. Superhydrophobic surfaces with a water contact angle greater than  $150^\circ$  and a sliding angle less than  $10^\circ$  have attracted tremendous attention during the last decade mainly because of their unique water repellent and self-cleaning properties [2-6]. Owing to their properties, superhydrophobic surfaces have various applications in a variety of industries. Surface wettability has been known to be controlled by surface energy and roughness [7, 8]. The main characteristic of these superhydrophobic surfaces is their roughness on the micro-

and nanometer scale. ZnO is one of the important II-VI groups of n-type semiconductors whose iconicity resides at the borderline between the covalent and ionic semiconductor. Zinc oxide (ZnO) is a well-known wide band gap semiconductor 3.37 with excitation energy 60meV at room temperature. ZnO nanostructures are extremely varied and include structures such as nanorods, nanopillars, nanowires, nanopropellers, nanonails and nanobridges [11], has been currently realized by various methods including catalytic growth via vapor-liquid-solid epitaxial, hydrothermal method, plasma-molecular beam epitaxy, template-based growth, etc. However, hydrothermal-assisted (HTA) method is more convenient over others as it is less expensive with easier composition control, large area deposition, and works at lower temperatures. On the other hand, small changes in

any hydrothermal parameters, such as temperature, pH, the molar ratio of the precursors, or even reaction time, generate profound influence on the final products. Moreover, using HTA method, ZnO nanostructures of different morphologies could be synthesized [12, 13]. The ZnO surface is intrinsically hydrophilic because of the strong adhesion of hydroxyl groups to its surface [14, 15]. Although, the hydrophobic behaviors of ZnO coatings with and without chemical modifications have been reported elsewhere [16–20], still there remains great curiosity about the wetting properties of ZnO coatings with various micro/nanostructures [21, 22], where can the conversion of intrinsically hydrophilic ZnO surface into superhydrophobic surface [23–24]. Such ZnO structures have inherent surface roughness, which should cause air to be trapped underwater droplets resulting in the majority of the droplet floating on a layer of air. The surface energy can be lowered through chemical modification, which affects the surface wettability and may be useful for producing superhydrophobic ZnO surfaces. There are many applications of ZnO structures for which superhydrophobic and self-cleaning properties are desirable to enhance their conventional functionality, including in outdoor optoelectronics, display devices, photovoltaic solar cells, and gas sensors [25, 26]. There are numerous reports from various laboratories on the wettability of micro/nano-structured ZnO coatings. For example, Gongping et al. reported the synthesis of hydrophobic nanoneedles and nanonails using hierarchical nanostructures of ZnO Cao et al. also synthesized superhydrophobic single-crystalline semiconductor In(OH)3 nanocubes with a static water contact angle (CA) larger than  $150^\circ$  by the amino acid-assisted hydrothermal process Hao et al. achieved WCA of  $\sim 157^\circ$  for X90 pipeline steel surface using a low-surface-energy modified ZnO micro-nano coating Saleema et al. modified the zinc oxide nano towers using stearic acid and

achieved high WCA and very low hysteresis. Srivastava et al. conducted the modification of PTFE incorporated ZnO coating to achieve the superhydrophobic surfaces. Nikhil et al. modified the zinc oxide using palmitic acid functionalized ZnO (PA-ZnO) nanoparticles and achieved high WCA. The aim of this work is develop novel, simple, highly efficient, and low-cost technique for fabrication ZnO superhydrophobic surfaces, and with low surface energy material modification using the hydrothermal method and an oleic acid selected with different weight ratios by drop casting method. The purpose for select oleic acid an eco-friendly, non-toxic and low-cost compound.

## 2. Experimental Section

### 2.1. Materials

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; purity of 98.5%) was obtained from Scharlau Spain. Hexamethylenetetramine (HMT,  $\text{C}_6\text{H}_{12}\text{N}_4$ ; purity of 99 %) and acetone ( $\text{C}_2\text{H}_6\text{O}$ ; purity of 99%) from Hi-media India. Absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) from the Netherlands were used as received. Oleic acid ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ ) and distilled water. The glass substrate was acquired from Yingke Optical Products.

### 2.2. Synthesis of ZnO Nanostructure

Hydrothermal method was used to synthesize the ZnO nanostructure. 0.1M ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and 0.1M of HMT was dissolved in 80ml of distilled water and was stirred for 10min to complete dissolution. The pH of the zinc nitrate solution was kept at ( $\sim 6$ ). The solution was dissolved in inside a glass autoclave and sealed tightly then placed in the oven at  $120^\circ\text{C}$  for one hour. Finally, the white precipitate was collected by centrifugation, repeatedly washed with distilled water and ethanol, and dried at  $80^\circ\text{C}$  for several hours.

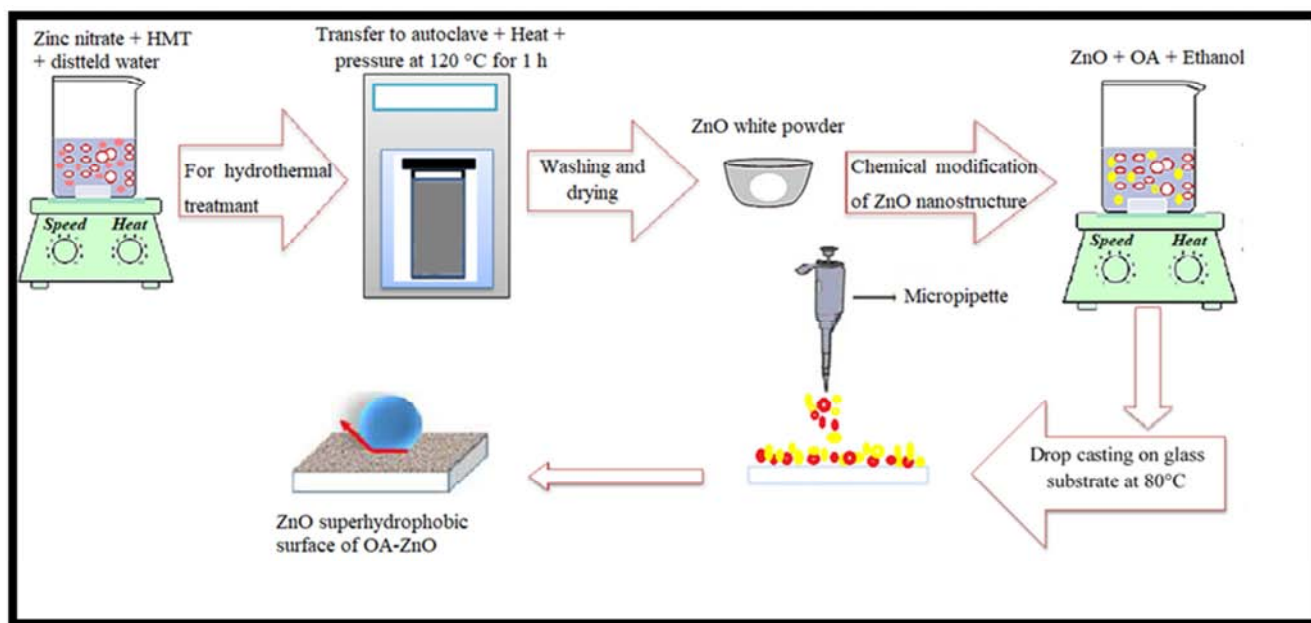


Figure 1. Photograph of the hydrothermal ZnO product.

### 2.3. Modification of ZnO with Oleic Acid

To obtain the bionic superhydrophobic surfaces, the as-prepared ZnO materials were modified by low-surface-energy oleic acid. In a typical modification procedure ZnO dry powder 0.2g and oleic acid with the different weight ratios to ZnO were dispersed in an ethanol solution 10ml with constant stirring for one hour at 100°C. The glass substrate was then cleaned with ethanol, acetone, and distilled water for several times to remove the residuals and impurities from the surface of the substrate. After homogenization, the solution was drop cast on a clean glass substrate using a micro-pipette and dried at 80°C. Figure 1 shows a photograph of the system used to prepare the ZnO by the hydrothermal method.

## 3. Characterization

The surface morphology of the as-prepared SHP ZnO surface was determined using a field emission scanning electron microscope (FESEM, Hitachi-S 4160-Japan). X-ray diffraction (XRD) analysis of the nanoarrays was performed using a Rigaku D/max-2500 using Cu K $\alpha$  radiation. To study the optical properties. The samples were tested for superhydrophobicity using a contact angle measurement setup which consisted of the arrangement for depositing a distilled water droplet (~5 $\mu$ l) on the sample surface, as shown in Figure 2. The water CAs of at least five different areas on the coating surface were measured and there were minimal variations, which is indicative of a uniform surface coating. A water drop was carefully applied on the surface. This process was monitored by a high-speed CCD camera with a setting of 25 frames per second.

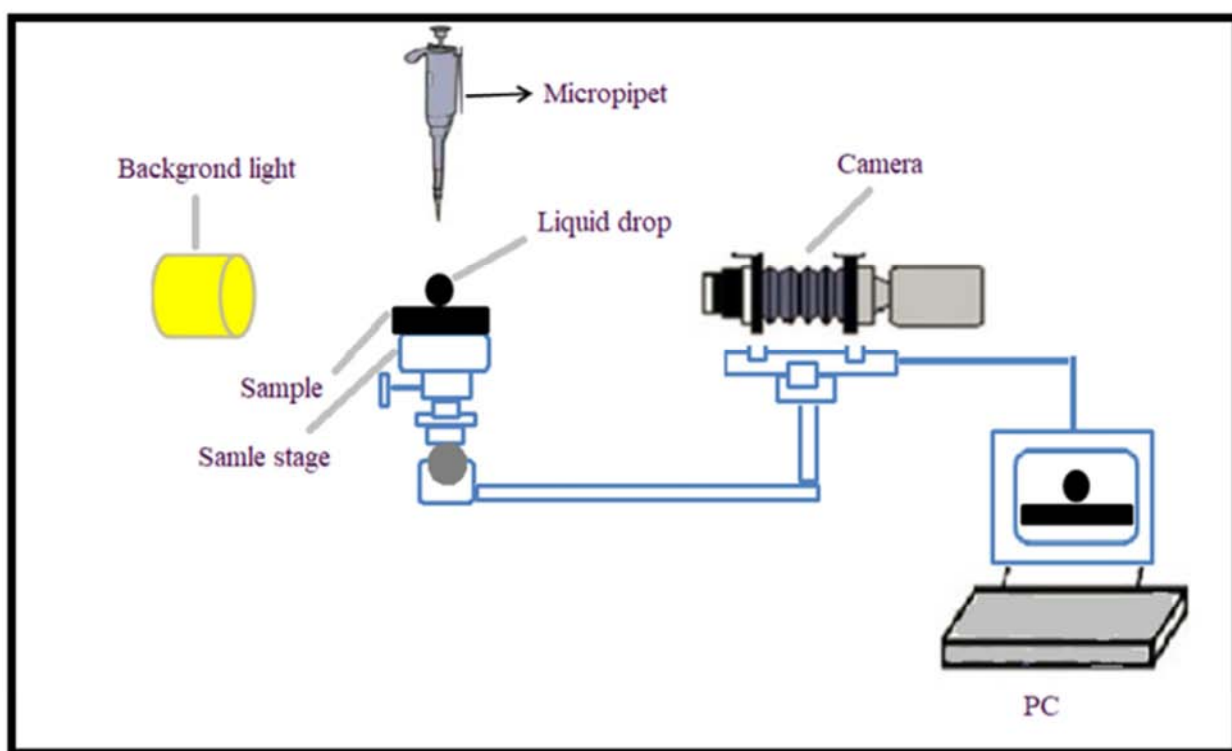


Figure 2. Experimental setup to measure Water CA.

## 4. Results and Discussion

Figure 3 shows the X-ray diffraction (XRD) pattern of the as-prepared ZnO sample. The diffraction peaks confirm the wurtzite hexagonal ZnO structure of the nanostructures. The observed peaks matching well with the reported (JCPDS) data of Zinc oxide, confirming the polycrystalline nature. The crystallite size was estimated as 30nm using the Debye-Scherrer equation. However, no diffraction peak from elemental Zn metal or other impurities were found in the sample.

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where D is the crystal size,  $\beta$  is full width at half maxima (FWHM) in radians,  $\theta$  is Bragg angle in degree and  $\lambda$  is X-ray wavelength. Figure 4 shows the FESEM images of ZnO surface morphologies without and with modification using oleic acid with different weight ratios. From the FESEM results, the result was hexagonal ZnO nanorods with relatively a homogeneous size and these hexagonal rods assembled in flower-like shape inside it are nanoparticles, the formation of small randomly distributed spherical shaped nanoparticles with 100 nm diameter, as shown in Figure 4 (A).

Figure 4 (B-F) shows the FESEM images of oleic acid modified ZnO coatings with different weight ratios. There was much change in the surface morphology of modified

samples after surface modification. Treatment with a lower weight of oleic acid 2 mg resulted in a non-uniform and partial oleic acid layer on a flower-like, the thickness of layers ranging from (59.11-171.15) nm, as shown in Figure 4 (B). While treatment with (4 mg and 6 mg) oleic acid yields a full coverage of the oleic acid layer, which produces the form of nanotubes and nanorods, respectively (Figure 4 (C, D)). Surface modification with (8 mg and 10mg) oleic acid resulted in heavy coverage of the fatty acid layer on the ZnO nanorods and nanotubes, respectively (Figure 4 (E, F)). The length, diameter and aspect ratio were measured by FESEM for all samples and observed when oleic acid weight increases the aspect ratio, as shown in Table 1. Figure 5 illustrates the plot between the effect of oleic acid and aspect ratio. The hydrophobic nature of pure (smooth) nano-ZnO and the water CA is measured to be  $138 \pm 1^\circ$ . To confirm that this superhydrophobic nature is dependent on the presence of oleic acid at the ZnO surface. Therefore, the water CAs increased steadily from  $147 \pm 2^\circ$  to  $154 \pm 2^\circ$  when the oleic acid weight percentage increased from 2 mg to 10 mg, as shown in Figure 6. Figure 7 illustrates the relationship between the effect of oleic acid and the water CA on superhydrophobic surfaces. The optical properties of as-grown ZnO nanostructures synthesized using the hydrothermal method at room-temperature and the data was recorded in the wavelength range of (250-900) nm demonstrated in Figure 8 (A). It is found that a distinct peak in the ultraviolet region about 354 nm (3.5 eV) is observed for pure ZnO nanoflowers before modification. The optical absorption spectra of ZnO nanotube after modification by oleic acid showed an absorption peak of about 344 nm (3.6 eV), as shown in Figure 8 (B). Thus, the optical band gaps of

the products are found to increase as aspect ratio increase, quantum confinement increase, and convert the hexagonal rods assembled in flower-like shape into a nanotube.

From a theoretical perspective, Young proposed an equation that states the liquid contact angle can only be applied to a smooth surface; thus, it doesn't consider the role of the surface roughness. However, the effect of surface roughness on wetting is included in the Wenzel model. According to the Wenzel approach, the liquid drop completely fills the grooves of a rough surface. The apparent water contact angle and intrinsic water contact angle are then related according to Wenzel's equation.

$$\cos \theta_{\text{rough}} = r \cos \theta_{\text{smooth}} \quad (2)$$

where,  $r$  is the ratio between the true surface area and its horizontal projection, and  $\theta_{\text{rough}}$  and  $\theta_{\text{smooth}}$  are the contact angle values on rough and smooth surfaces, respectively. This regime provides hydrophobic inter faces with contact angles less than  $120^\circ$ ; however, it cannot impart superhydrophobicity. The Cassie-Baxter model is based on the assumption that air may be trapped in the grooves of the rough surface and the water drop is partially supported by the air to enhance the hydrophobicity. In the Cassie state, the apparent water contact angle is related to the intrinsic water contact angle of the solid surface by the following equation [35]:

$$\cos \theta_{\text{rough}} = f (\cos \theta_{\text{smooth}} + 1) \quad (3)$$

where,  $f$  is the area fraction of the liquid and solid on the surface.

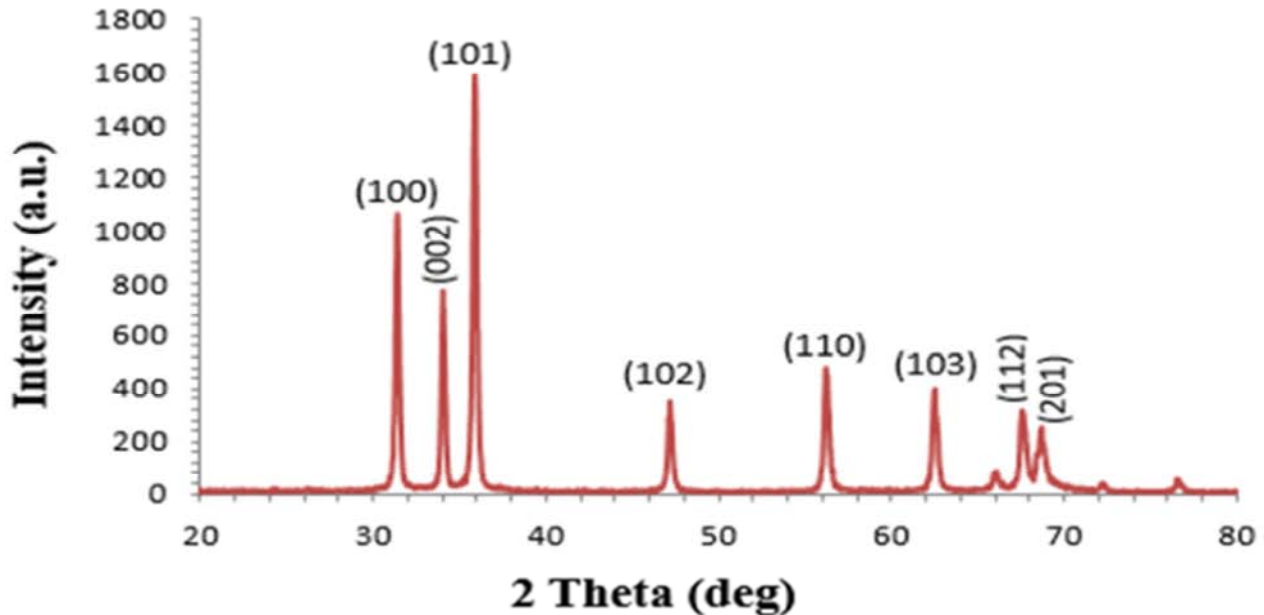
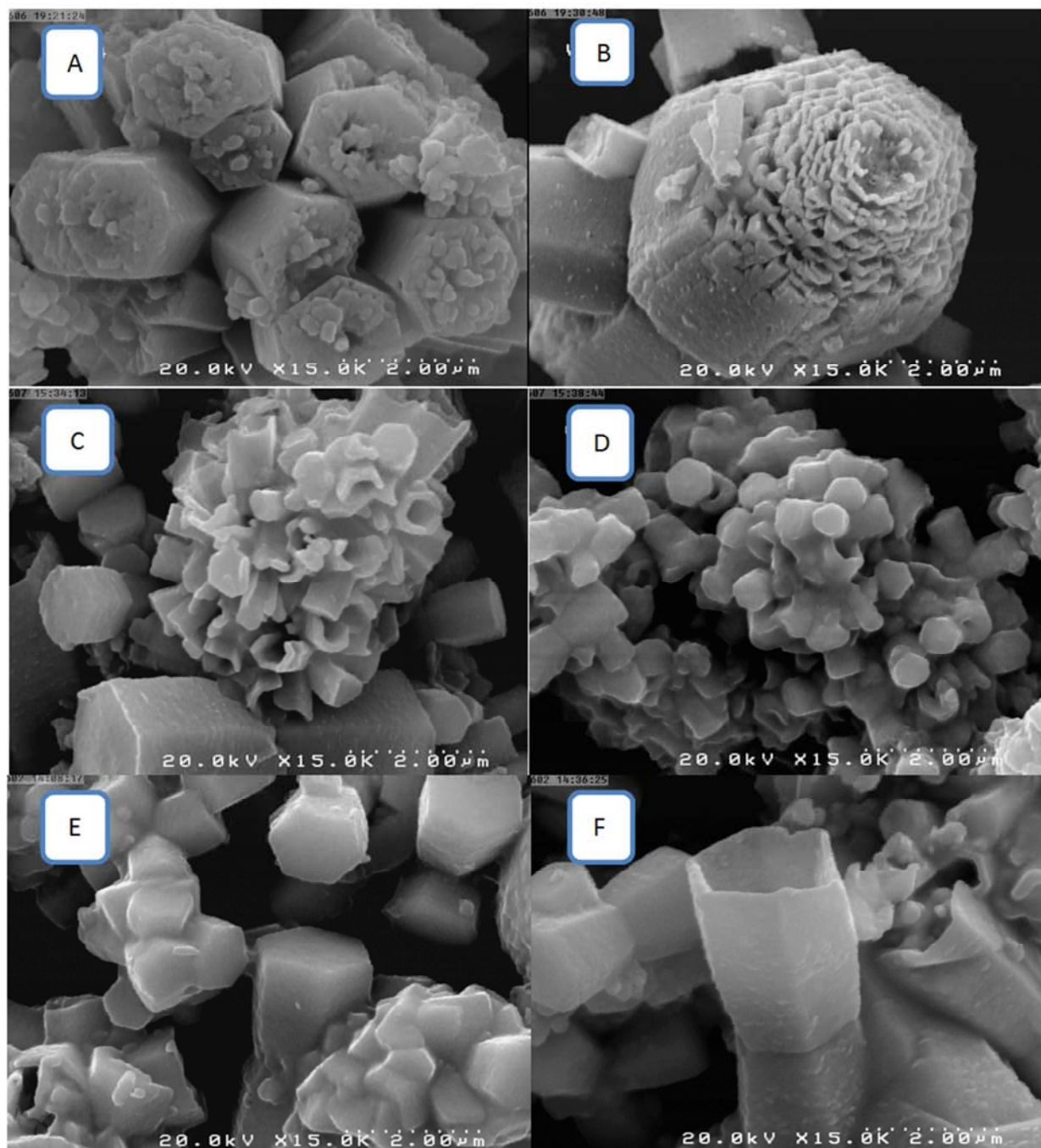


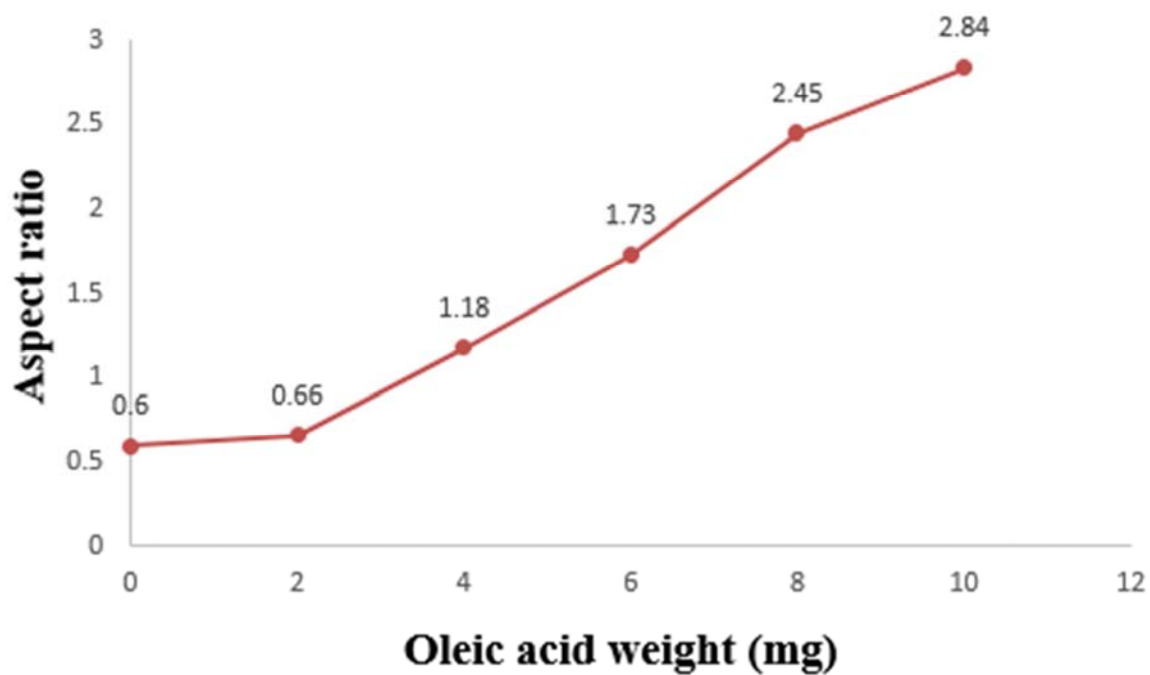
Figure 3. X-ray diffraction pattern of as-prepared ZnO sample by hydrothermal method.



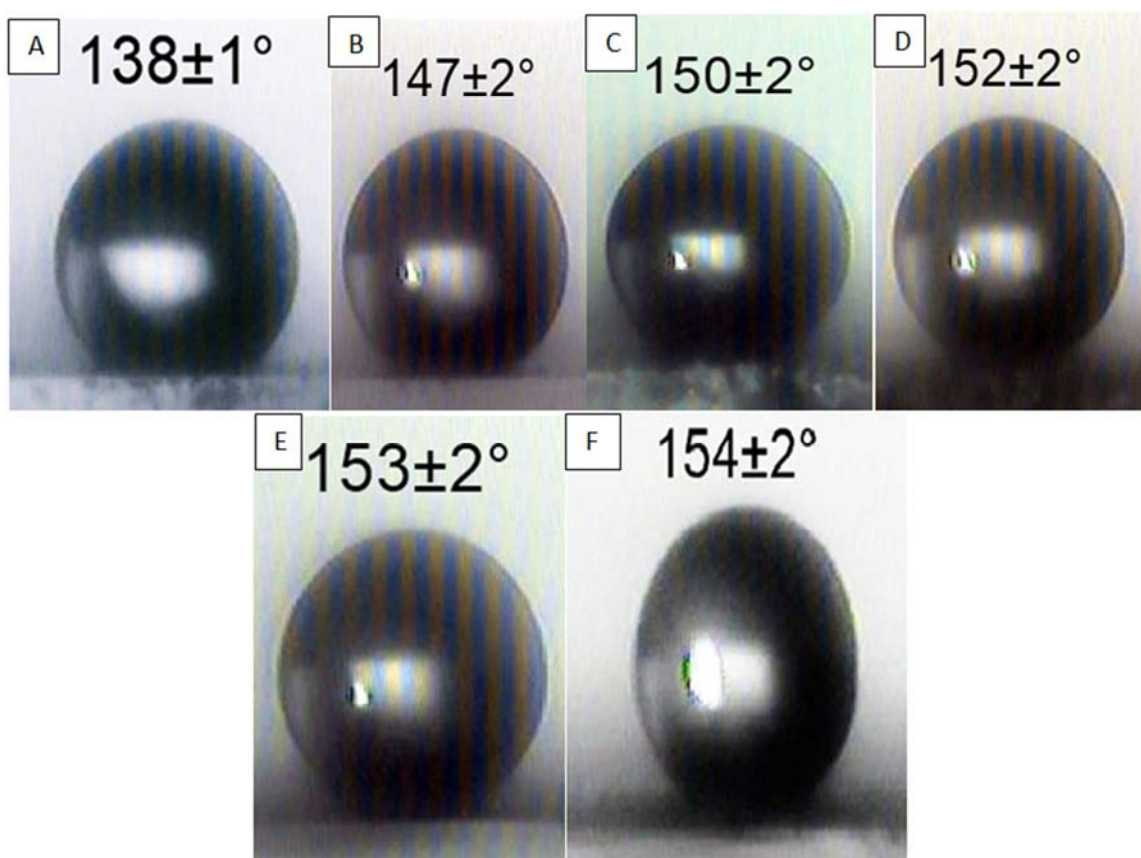
**Figure 4.** FESEM images of ZnO surface morphologies (A) before, and modification using oleic acid with different weight ratios (B) 2mg, (C) 4mg, (D) 6mg, (E) 8mg, (F) 10mg.

**Table 1.** Length, diameter, and aspect ratio of ZnO nanostructures at various oleic acid weight.

Oleic acid weight (mg)	Length (nm)	Diameter (nm)	Aspect ratio
0	810.73	1330.04	0.6
2	1616.42	2413.27	0.66
4	472.45	398.90	1.18
6	892.22	648.48	1.37
8	1640.20	667.44	2.45
10	2894.44	1081.41	2.84



**Figure 5.** The plot of the aspect ratios of as-grown ZnO nanostructure as a function of weight.



**Figure 6.** Water contact angle images for oleic acid weight (A) 0 mg (B) 2 mg (C) 4 mg (D) 6 mg (E) 8 mg and (F) 10 mg.

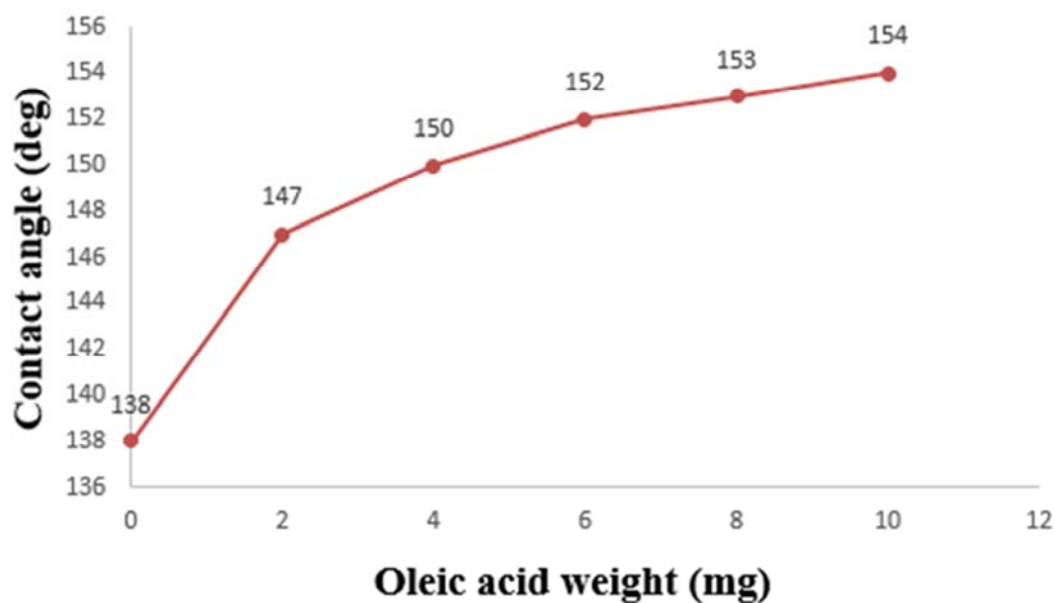


Figure 7. Relationship between the effect of oleic acid and the water CA on superhydrophobic surfaces.

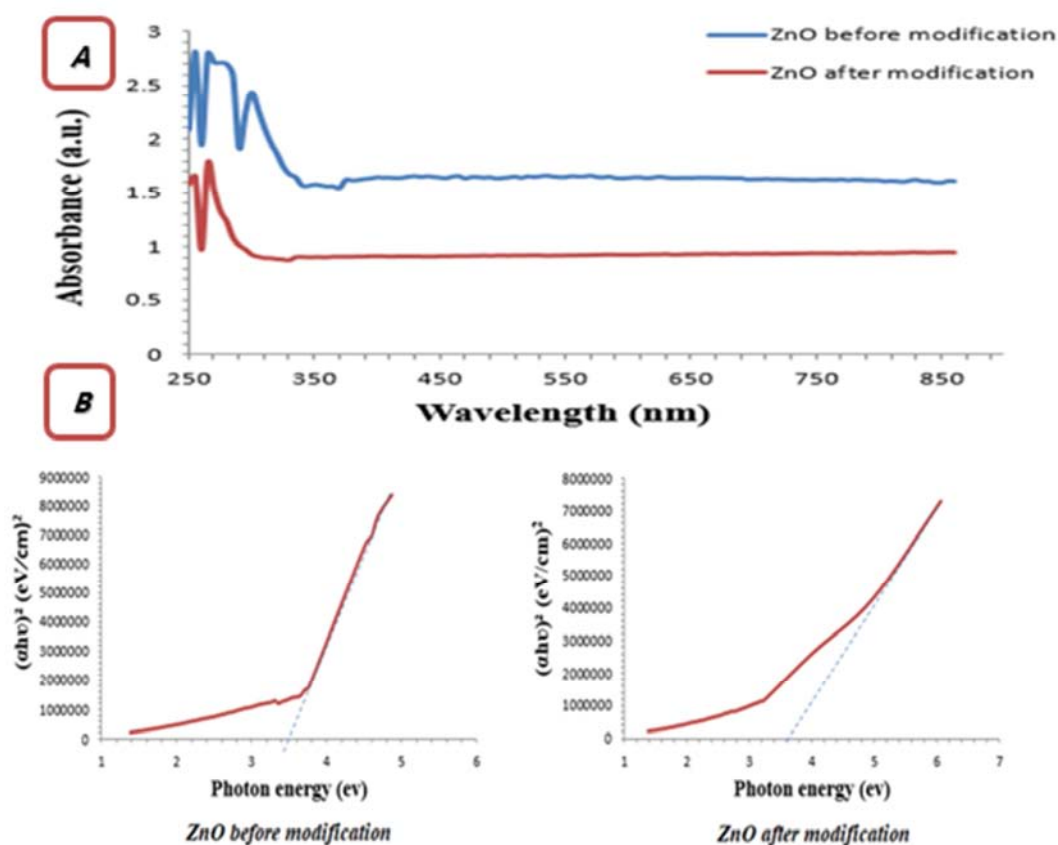


Figure 8. Typical UV-vis spectra of ZnO before and after modification (A) Absorbance, (B) Energy band gap.

## 5. Conclusions

In summary, a facile method selected for fabricating a superhydrophobic surface with high chemical stability and good self-cleaning by a simple, highly efficient, and low-cost

using hydrothermal method to be applied in commercial and industrial applications. Superhydrophobic surfaces could be created through a simple surface modification with oleic acid. The wettability of the ZnO surface was tuned by changing the oleic acid weight; it demonstrated different static wetting behaviors depending on the oleic acid weight.

The water CA of the prepared superhydrophobic ZnO surface was  $154 \pm 2^\circ$ . The superhydrophobic ZnO surface exhibits excellent self-cleaning property compared with the pure ZnO surface. The results indicate that precise control of the surface chemical composition and micro-/nanostructure is necessary to attain high water contact angles, which is paramount for designing practical superhydrophobic and self-cleaning technology. These features make use this method to be very suitable to apply on other metals oxide to fabricate superhydrophobic surfaces through the selection of an appropriate fatty acids, and very suitable for practical application in many areas, especially in medical devices.

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