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# Effect of modification of zinc oxide nanostructures on contact angle

# Efecto de la modificación de nanoestructuras de óxido de zinc sobre ángulo de contacto

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**Abstract**

The hydrophobic coatings are one of the most used processes to prevent the deterioration of materials and increase its lifetime, since they have non-stick, low friction, anti-wetting, high and low temperature resistance, chemical and dielectric properties, etc. This work presents the chemical production of zinc oxide (ZnO) nanostructures that were deposited on glass substrates by two methods: spin-coating and dip-coating. The doped substrates were modified by temperature and exposure to ultraviolet light (UV). The contact angle of the surface was measured after making some modification, revealing an initial change compared to the uncoated substrate. Later, the angles were varied, comparing between the two deposition methods. The higher contact angle was presented by spin-coating sample, after rising its temperature and a first exposure to UV light; an increase of 30% was observed in comparison to the uncoated substrate; In contrast, the smallest angle was obtained in dip-coating sample after raising its temperature, reducing around 55% of its size compared to the uncoated substrate.

**Hydrophobicity, Zinc oxide, Nanostructures**

**Resumen**

El uso de recubrimientos hidrofóbicos es uno de los procesos más empleados para evitar el deterioro de los materiales y prolongar su vida útil ya que poseen propiedades anti-adherentes, baja fricción, anti-humectantes, resistentes a altas y bajas temperaturas, resistencia química y dieléctrica, entre otras. El presente trabajo se basa en la producción química de nanoestructuras de óxido de zinc (ZnO) que se depositaron sobre sustratos de vidrio por dos métodos diferentes: spin-coating y dip-coating. Los sustratos dopados fueron modificados mediante temperatura y exposición a luz ultra violeta. Se caracterizó midiendo el ángulo de contacto de la superficie después de realizarle alguna modificación, lo anterior mostró un cambio inicial comparado con el sustrato sin recubrir, posteriormente los ángulos fueron variando obteniendo una comparativa entre los dos métodos de deposición. El mayor ángulo de contacto lo presentó la muestra realizada por spin-coating después de elevar su temperatura y una primera exposición a luz ultravioleta, aumentó un 30% contra el ángulo medido en el sustrato sin recubrir; de manera contraria el ángulo más pequeño se obtuvo en el sustrato por dip-coating después de elevar su temperatura, este redujo aproximadamente un 55% de su tamaño con respecto al sustrato sin recubrimiento.

**Hidrofobicidad, óxido de zinc, nanoestructuras**

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## Introduction

The support provided by nanotechnology for the design and development of new materials, modifying their properties based on shape, size and functionalization, has opened new horizons in new material properties [1, 2].

*Hydrophobicity and Hydrophilicity*

The Greek roots define hydro as water, philia as affinity, and phobia as lack of affinity, thus forming hydrophobicity (water repellency) and hydrophilicity (water affinity). A surface is considered hydrophobic when the angle formed between the surface and a fluid exceeds 90°, below 90° the surface is hydrophilic [3].

*ZnO nanostructures*

Zinc oxide is an attractive compound for various applications in nanotechnology due to its unique qualities and physical and chemical properties. The procedure to grow nanostructures is simple and inexpensive, therefore, there are multiple synthesis methods such as chemical vapor deposition, chemical synthesis, physical vapor deposition, green chemistry, among others [4, 5]. Zinc oxide shows a particularity, since the inclination it forms with the surface of liquids is nanostructured, it shows physicochemical properties such as hydrophobicity or hydrophilicity [6].

As zinc oxide nanostructures grow, they modify its behavior by increasing or decreasing their surface area. Exposure of these compounds to ultraviolet light and temperature can modify their wettability, causing a change of state [7].

These small structures can be used for the growth of various nanostructures with similar properties, but different dimensions. For example, nanowires belong to the 1D classification because one of their dimensions is in the nanometric order, although it extends to micrometers [8].

## Methodology

The synthesis of the nanostructures was chemically conducted with zinc acetate and sodium chloride, both diluted in methanol. This solution was kept under stirring for two hours at a controlled temperature of 60 °C.

Once the substrates were clean, 10 μL of the solution were deposited by spin coating at 10,000 rpm; additionally, dip coating was performed with a single immersion in the solution. Later, both were left drying at room temperature.


**Figure 1** Spin and dip coating process

Both samples were modified increasing temperature and irradiating them with ultraviolet light, to change the contact angle after each process.

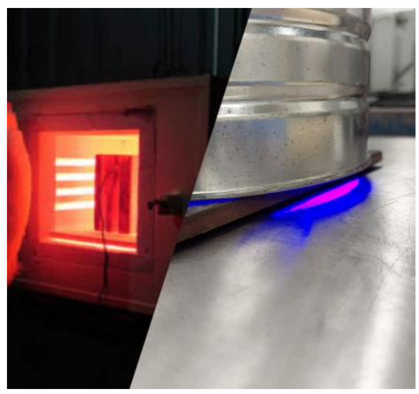

**Figure 2** Procedure to modify the behavior of nanostructures

The samples were placed in a furnace at 300 °C for 90 minutes; once the sample cooled, its contact angle was measured. Next, samples were subjected to ultraviolet light for 60 minutes, again measuring the contact angle; finally, further irradiation for 90 minutes were conducted, measuring the contact angle.

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**Figure 3** Drop of water photograph for contact angle measurement

When all contact angles were acquired, measurement in ImageJ software was conducted. Similarly, the angle was measured in clean substrate without doping.

## Results

The contact angles changed significantly with the deposition of nanostructures. Figure 4 shows the measurement of a drop on the surface of uncoated substrate, observing an angle of 63.064°.

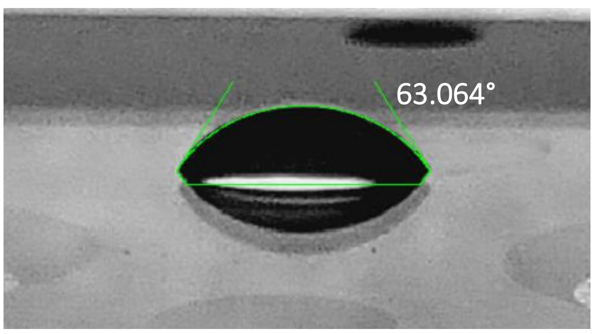


**Figure 4** Unmodified substrate contact angle

The samples made by spin coating presented large angles, however, a decrease in the angle occurred as the irradiation time with ultraviolet light increased.

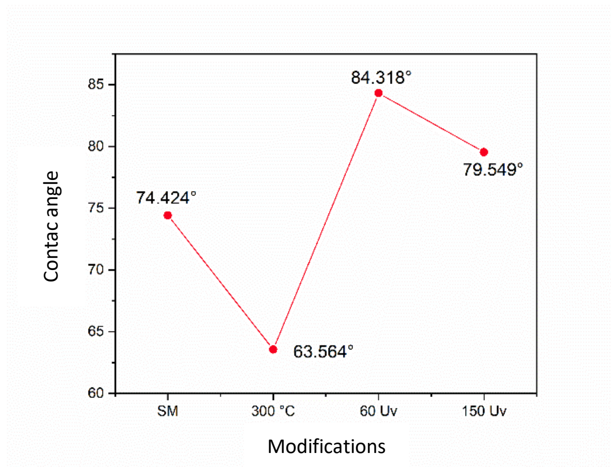


**Figure 5** Contact angles behavior of spin-coating samples

As can be seen in Figure 6, the shape of the droplet on the surface changed with the modifications, Figure 6b shows a more elongated droplet with the lowest contact angle; on the other hand, the highest angle is presented in figure 6c where a drop with the shape of a half sphere is observed.

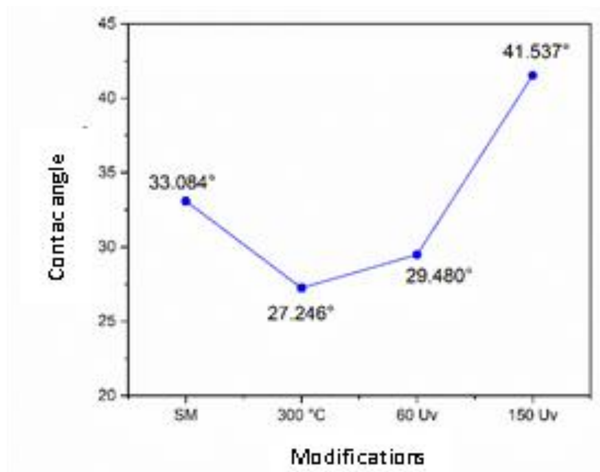


**Figure 6** Measurement of the contact angles of the samples by spin coating. a) sample with zinc oxide nanostructures, b) sample after 90 min at 300 °C, c) sample after 60 min exposed to ultraviolet light, d) sample after 150 min exposed to ultraviolet light

The samples that were coated by dip coating showed an immediate decrease in the contact angle in comparison to uncoated substrate, however, with the modification processes, the angle increase, as shown in figure 5.

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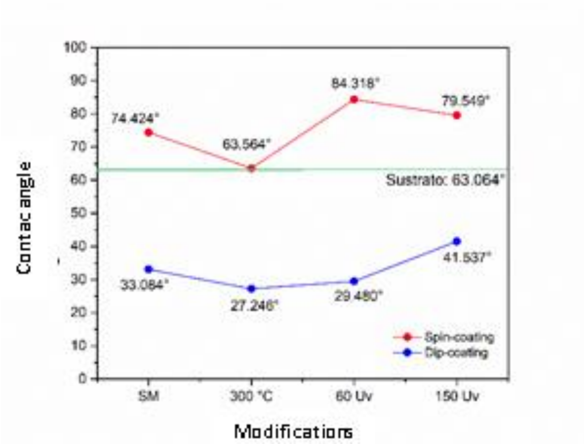


**Figure 7** Contact angles behavior of dip-coating samples

The shape of the droplets on the surface changes significantly after the modifications. Figure 8 shows elongated drops with little height, giving measurements below 45°. Fig. 7d shows the greatest height, therefore, the highest angle in these 4 measurements.

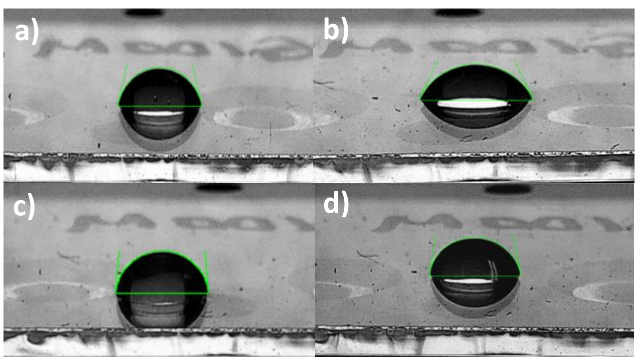


**Figure 8** Measurement of the contact angles of the samples by dip coating. a) sample with zinc oxide nanostructures, b) sample after 90 min at 300 °C, c) sample after 60 min exposed to ultraviolet light, d) sample after 150 min exposed to ultraviolet light

The change in the value of the contact angles is visible by the shape of the drops, figure 9 shows the contact angles behavior compared to uncoated substrate.

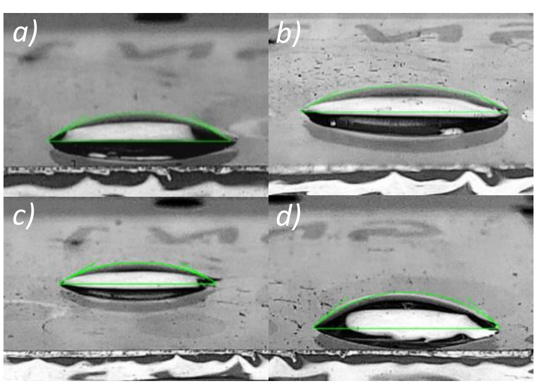


**Figure 9** Change in contact angles against uncoated substrate

The green reference line corresponds to the measurement of the angle obtained on the clean substrate. The variation of the measurements is significant, the dip-coating sample presents low values, far from the reference line; whereas the spin-coating sample presents values above reference, but not reaching the required 90° to be considered as hydrophobic.

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## Conclusions

The results revealed a superficial change in the samples explained by the procedure followed to deposit the nanostructures and the modifications conducted in each sample. The water drop behavior on the clean and doped substrate changes instantly. The increase and decrease in the contact angle are attributed to the treatment applied to the nanostructures. Changing the properties through variations in temperature or irradiation can generate several applications. In addition, comparing two methods for the deposition of solutions gives the opportunity to continue with the investigation and be able to obtain larger angles.

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