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Variation in the contact angle of zinc oxide nanostructures with the passage of time

Variación en el ángulo de contacto de nanoestructuras de óxido de zinc con el paso del tiempo

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Abstract

The development of clean materials has increased; these materials present a surface modification that makes them neat and easy to clean. The direct improvement in the impermeability of materials is generated by manipulating the structures present on the surfaces, generating self-cleaning coatings (hydrophobic surfaces). The modification can be developed by superficially synthesizing nanostructures of specific shapes on some solid that prevent the passage of liquids between them, for example, zinc oxide nanowires that exhibit a high contact angle due to their geometry. The synthesis of these nanostructures is low cost and simple, making it a viable alternative to achieve hydrophobic surfaces that are self-cleaning. The present work shows how the synthesis factors of these nanostructures impact their contact angle. Hydrophobic contact angles were obtained in most samples and nanostructures averaging 290 nm and average lengths of 2.2 μm.

Contact angle, Hydrophobicity, Zinc Oxide

Resumen

El desarrollo de materiales limpios ha incrementado, estos presentan una modificación superficial que los vuelve pulcros y de fácil aseo. La mejora directa en la impermeabilidad de los materiales se genera al manipular las estructuras presentes en las superficies generando revestimientos autolimpiantes (superficies hidrofóbicas). La modificación se puede desarrollar al sintetizar de manera superficial sobre algún sólido nanoestructuras de formas específicas que impidan el paso de los líquidos entre ellas, por ejemplo, los nanocables de óxido de zinc que exhiben un alto ángulo de contacto por su geometría. La síntesis de estas nanoestructuras es de bajo costo y sencilla por lo que se vuelve una alternativa viable para lograr superficies hidrofóbicas que sean autolimpiantes. El presente trabajo muestra como los factores de síntesis de estas nanoestructuras impactan sobre su ángulo de contacto. Se obtuvieron ángulos de contacto hidrofóbicos en la mayoría de las muestras y nanoestructuras de promedios de 290 nm y longitudes promedio de 2.2 μm.

Ángulo de contacto, Hidrofobicidad, Óxido de Zinc

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1. Introduction

Intermolecular interactions maintain the contact between a solid and a liquid surface, this is known as wetting. To carry out the analysis of this characteristic, the contact angle is used, which is established when there is an equilibrium between cohesive and adhesive forces of a liquid [1].

The contact angle classifies surfaces as hydrophobic due to their lack of affinity for water or hydrophilic due to their affinity for water; this tool makes use of the degrees that a drop of water presents when in contact with a solid [2].

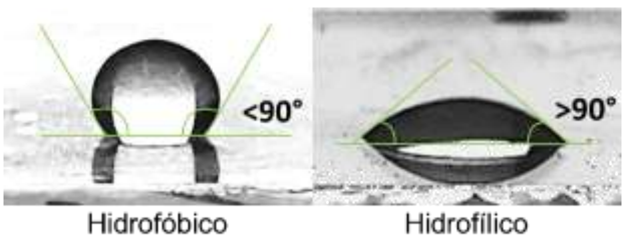

Figure 1 Classification of contact angles

Hydrophobic surfaces are found when the tangent of the droplet exhibits an angle greater than or equal to 90°, the opposite is the case for hydrophilic surfaces which exhibit an angle less than 90° (figure 1). These parameters have been accepted since on surfaces with angles less than 90° when the droplet is removed from the surface it gives a small residue and on surfaces with an angle equal to 90° the droplet is removed intact. [3].

The influence of the contact angle will depend on the characteristics of the solid with which it comes into contact. Materials may or may not allow liquids to pass on their surface depending on their impermeability, this is limited by the size of the openings of the surface structures, as with larger openings water can spread between them [4].

Solid surfaces can be modified to change their impermeability, for example, with the use of nanostructures. The synthesis of these materials has been considered as an important step in the generation of clean materials with anti-stain properties or self-cleaning coatings [5].

The improvement of this property in materials allows to obtain easy-to-clean and neat surface finishes, which is why nanocoatings open the way to a new concept of protection [5]. Within the nanometre sizes there are various geometries, sizes and dimensions that will have unique properties. Self-cleaning materials require structures with specific crystallographic orientations, for example, wurtzite-type zinc oxide nanowires that have c-axis oriented non-polar surfaces with a divergence in their surface energy producing hydrophobic or hydrophilic surfaces [6].

Manipulation of crystallographic orientations can generate important changes on the surface of zinc oxide nanostructures, this manipulation will depend on synthesis factors such as seed, pH and growth time [7].

The first step for the generation of zinc oxide nanowires is the synthesis of a seed that functions as an anchor in the solid, depending on the characteristics of the seed, which will favour the homogeneity of the nanowire growth. It is important to maintain a dense and strong seed with good dispersion and without agglomerations, generally the chemical synthesis is the most used, likewise the way in which the seed is placed on the solid will influence its final characteristics [8].

After the placement of the seed, the quality of the nanowires will depend on the method used for their growth, one of the methods that offers good results is the hydrothermal method due to its low cost, simplicity and because it avoids the agglomeration of the nanostructures. This method is affected by the pH of the solution, which determines the geometry of the nanostructure; a pH of 7 favours the growth of hexagonal structures [9]. The growth time of the nanowires depends on factors such as pressure and temperature control, within the first hour of processing the base of the nanowires is synthesised, after that the growth becomes vertical. [10].

2. Methodology to be developed

Substrate

Conventional glass obtained from optical microscopy slides, washed with neutral liquid soap, distilled water, alcohol and acetone, dried with compressed air.

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Seed

The seed of the zinc oxide nanowires is chemically synthesised using zinc acetate and sodium hydroxide dissolved in methanol, left to stir at 60°C for two hours. It is allowed to cool to room temperature.

Seed deposition

The seed is deposited on the substrates by two different methods, spin-coating with a constant speed of 3,000 rpm and varying the rotation time of 10, 20, 30, 40, 40, 50 and 60 seconds; the second method is dip-coating using 5, 10, 15, 20, 25 and 30 immersions.

Growth of zinc oxide nanowires

Zinc oxide nanowires are grown by the hydrothermal method using a mixture of zinc nitrate and hexamethylenetetramine dissolved in water. The substrates with the seed are immersed in the mixture, covered and heated for 4.5 hours at 90°C. After this process they are washed with distilled water and left to dry at room temperature.

3. Results

One of the samples was characterised by energy dispersion analysis with the seed obtained by chemical means, figure 2 shows the elemental analysis, the seed elements zinc and oxygen are present, as well as the substrate element silicon.

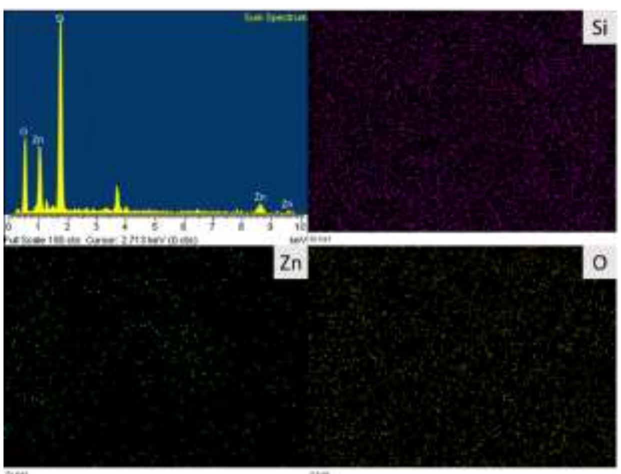

Figure 1 EDS of the seed on the substrate

The samples were also characterised by scanning electron microscopy after the growth of the zinc oxide nanowires, as shown in figure 3, hexagonal nanostructures were obtained.

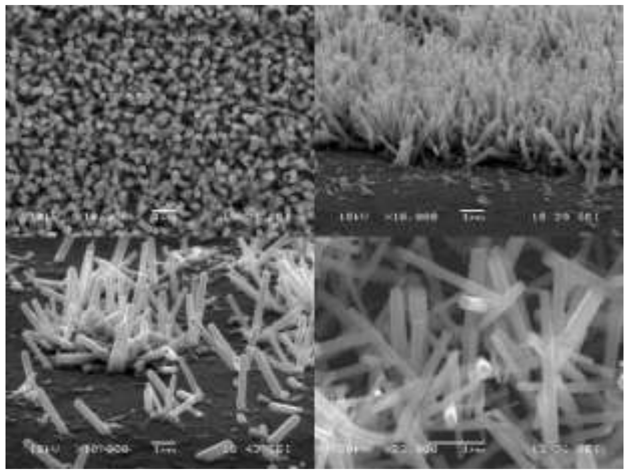

Figure 2 Zinc oxide nanowires on a glass substrate

Few images of the grown nanowires were obtained as the substrate used hinders taking good quality images, however, some images were selected to make vertex-to-vertex measurements of each hexagon. A total of 466 structures were measured, calculating an average of 291.6 nanometres, and in some of the images it was possible to observe the base of the nanowires. 50 measurements were taken, obtaining an average of 2.21 microns in length.

The contact angle of the seed, the zinc oxide nanowires on the day of their synthesis and the zinc oxide nanowires 40 days after their synthesis of the samples with seed deposited by spin-coating were analysed (figure 4).

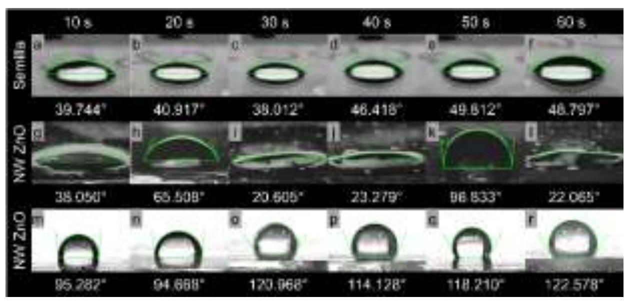

Figure 3 Seed contact angles by spin-coating with 3,000 rpm varying deposition time (a-f); contact angles of zinc oxide nanowires on the same day of their synthesis (g-l); contact angles of zinc oxide nanowires 40 days after their synthesis (m-r)

The seed exhibits angles between 38° to almost 50°, once the zinc oxide nanowires are grown on the surface the angles change as in 4 out of 6 cases the angle decreases. The samples were left to stand in a dark environment for 40 days to measure their contact angle again, all surfaces exceeded 90°.

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The contact angle of the samples with seed deposited by dip-coating was measured, as well as the angle of the seed of the zinc oxide nanowires on the day of synthesis and 40 days after synthesis (figure 5).

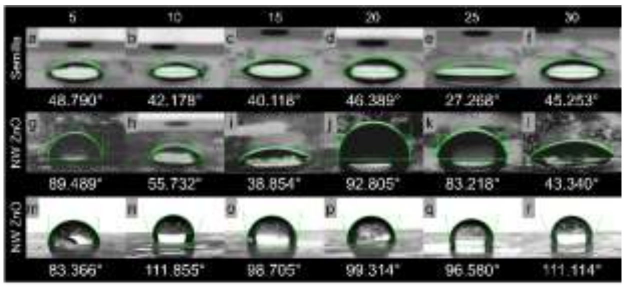

Figure 4 Contact angles of seeds by dip-coating with different immersions (a)5, b)10, c)15, d)20, e)25, f)25); contact angles of zinc oxide nanowires on the same day of their synthesis (g-l); contact angles of zinc oxide nanowires 40 days after their synthesis (m-r); contact angles of zinc oxide nanowires 40 days after their synthesis (m-r); contact angles of zinc oxide nanowires 40 days after their synthesis (m-r)

This set of samples has hydrophilic angles when only the seed is present, it changes when generating the growth of the zinc oxide nanowires, this change is very varied for each sample and after 40 days of resting in a dark environment 5 of the 6 samples are above 90°.

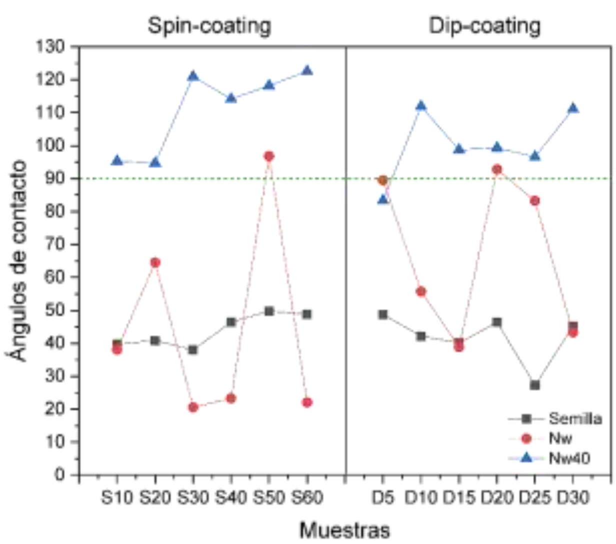

Figure 5 Graph of the changes in contact angles

Figure 6 shows graphically the change in contact angles, it is visible how over time the substrates tend to increase their contact angle generating hydrophobic surfaces

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5. Conclusions

The method of seed deposition directly influences the homogeneity of the seed on the surface and how the contact angle changes after the growth of the zinc oxide nanowires.

The hydrothermal method as a low-temperature zinc oxide nanowire growth process favours the formation of hexagonal structures at an average of 290 nm and average lengths of 2.2 microns.

The increase of the contact angle increases if the samples are left at rest and in a dark environment.

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