

## Evaluation of the photocatalytic performance of ZnO nanostructures obtained by different synthesis methods

## Evaluación del desempeño fotocatalítico de nanoestructuras de ZnO obtenidas por diferentes métodos de síntesis

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### Abstract

The industrial revolution gave way to the generation of pollutants that are harmful to the environment and that have been increasing, contaminating bodies of drinking water for this reason, solutions are currently being sought to eliminate some of these contaminants, such as dyes from the textile industry. This work describes the synthesis by different methods (physical and/or chemical) of zinc oxide nanostructures: nanopowders, nanowires and thin films, to evaluate their potential in the degradation of methyl orange in aqueous medium. The characterization of the materials was carried out by scanning electron microscopy and UV-vis spectrophotometry.

**Photocatalysis, Zinc Oxide, Nanostructures**

### Resumen

La revolución industrial dio paso a la generación de contaminantes nocivos al medio ambiente y que han ido en aumento, contaminando cuerpos de agua potable; por esta razón actualmente se están buscando soluciones para eliminar algunos de estos contaminantes como los colorantes de la industria textil. Este trabajo describe la síntesis por diferentes métodos (físicos y/o químicos) de nanoestructuras de óxido de zinc: nanopolvos, nanocables y películas delgadas, para evaluar su potencial en la degradación del naranja de metilo en medio acuoso. La caracterización de los materiales se realizó por microscopia electrónica de barrido y espectrofotometría UV-vis.

**Fotocatálisis, Óxido de Zinc, Nanoestructuras**

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## 1. Introduction

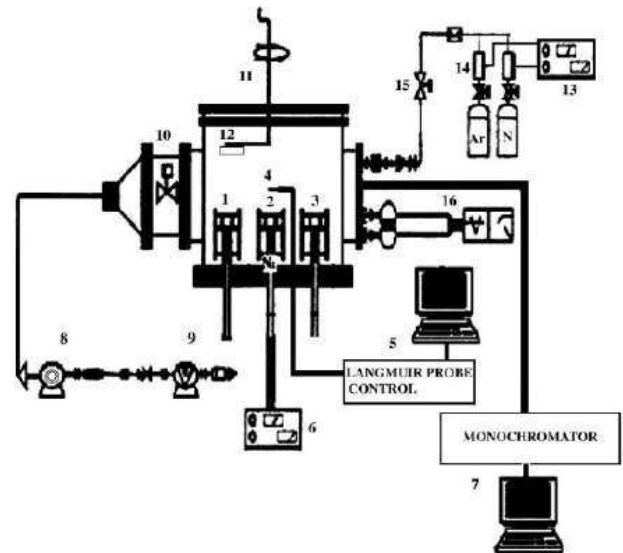
The industrial revolution had a major impact on many aspects of society and technology, including the textile industry, which led to the generation of pollutants and waste, such as methyl orange (MN), a synthetic dye.

As the global population continues to grow, production rates will continue to rise and with it, so will the generation of pollution, these pollutants generally end up in aquatic systems and have a detrimental effect on both the ecosystem and human health, therefore, Nanotechnology has also proven to be a versatile tool, given that throughout its history it has confirmed that it has the potential to adapt to and solve industrial problems by generating new materials with unique properties [1].

Nanotechnology offers more efficient alternatives for the degradation of pollutants through the use of different nanostructures [1]. The synthesis of these nanomaterials can be obtained by two ways, chemical and physical, however, there is also the possibility of using both for the modification of these same, one of the chemical methods is by coprecipitation, this method allows us to obtain nanomaterials and consists of the simultaneous precipitation of 2 or more chemical substances, which are mixed in a single solution, from the addition of a third reagent that generates the precipitation, for this there must be similarities between the compounds to use the growth of nanostructures depends on the type of precursor salt to use and the pH of the final solution [2].

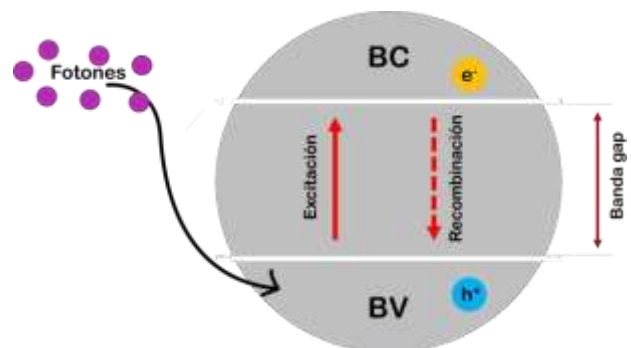
Another chemical method is hydrothermal in which a metallic precursor is used in a solvent, which being a solvent, which being a hydrothermal process must be dissolved in water, this solution will be brought to its boiling point and maintained at a constant pressure [3].

And finally by physical means is the physical deposition of steam by reactive magnetron that allows us to obtain thin films [4] from these methods we can obtain different nanostructures, classified according to their dimensions: 0D, 1D, 2D and 3D [5].



**Figure 1** General schematic of the reactive magnetron sputtering equipment [4]

In addition, nanomaterials can be functionalised to achieve the decomposition of specific pollutants, since different catalytic or absorbing agents can be incorporated into their structure. Photocatalysis is a process that is based on the energy interactions between the bands (BC: valence band, gap band and BV: conduction band) and for photocatalysis, semiconductor nanomaterials are required that can act as catalysts and with the interaction of a photon can act as a photocatalyst and can be used in heterogeneous photocatalysis for the degradation of pollutants present in water. (fig. 1).



**Figure 2** General mechanism of photocatalysis

Heterogeneous photocatalysis occurs when the amount received by the photon is equal to or greater than the gap band, allowing the electron to rise to the higher energy conduction band and holes in the valence band of the catalyst [6].

Zinc oxide has proven to be an efficient nanomaterial for the degradation of organic compounds, since it is a semiconductor that has a gap band of approximately 3.36 eV, has a high stability and a good quality in thermal conductivity, these properties have allowed it to be used in various branches of technology, such as optoelectronics, cosmetics industry and since it has a low toxicity, is biodegradable and biocompatible it can be used in medicine, as well as for water treatment by having photocatalytic properties [7, 8].

## 2. Methodology to develop

The experimental part was carried out in 3 stages: first, synthesis of nanopowders by co-precipitation; second, synthesis of thin films by plasma-assisted physical vapour deposition (PVD) and finally, growth of zinc oxide nanostructures by hydrothermal method. For the synthesis of the nanopowders (fig.2), zinc acetate dihydrate dissolved in hydrochloric acid and hydrochloric acid were used hydrochloric acid and an ammonia hydroxide solution were used for the synthesis of the nanopowders (fig.2), mixed under gentle stirring until a pH between 8-10 was obtained. The precipitates were allowed to cool to room temperature, filtered and washed with distilled water and placed in an oven at 100°C for 5 hours.



**Figure 2** Nanostructured zinc oxide powders

The thin films were obtained in a PVD reactor using a high purity zinc target (99.9999%), argon gas and oxygen. An architecture with a zinc adhesion layer was generated for 10 seconds, then a zinc oxide layer was deposited for 10 seconds (fig.3).



**Figure 3** Architecture of the PVD-synthesised thin film

Finally, for the growth of zinc oxide nanostructures, thin films obtained by PVD were used as seeds. For the hydrothermal method, a solution of hexamethylenetetramine and zinc nitrate was used; the seeds were immersed in this mixture and put in the oven for 6 hours at a temperature of 90°C, finally they were washed with distilled water and dried at room temperature. (fig.4).



**Figure 4** Architecture for obtaining zinc oxide nanowires by PVD/hydrothermal PVD

For the photocatalytic tests, a 20 ppm solution of methyl orange was prepared and a ten-point calibration curve was performed (fig. 5). Using a 365 nm UV lamp, the samples were exposed for 30, 60 and 120 minutes. Finally, the photocatalytic performance of each of the nanostructures was evaluated by UV-vis spectrophotometry, characterised by scanning electron microscopy (SEM) and the contact angle was measured.

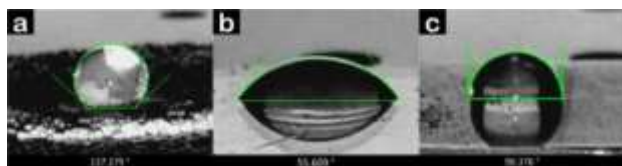
## 3. Results

Three nanostructures were obtained, figure 6 shows the powders (fig. 5a), the substrate surface with the film only (fig. 5b) and the substrate surface after the synthesis of the nanowires. (fig. 5c).



**Figure 5** Nanostructures obtained. a) ZnO powders, b) ZnO thin film and c) ZnO nanowires

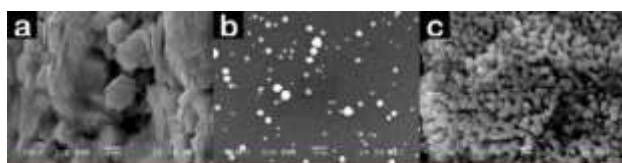
The nanostructures were characterised by Uv-vis spectrophotometry, scanning electron microscopy and contact angle



**Figure 6** Contact angle of zinc oxide nanostructures. a) powders, b) thin film and c) nanowires

As can be seen in figure 6 the contact angle of the 3 nanostructures is different, two are above  $90^\circ$  (hydrophobic) and one is below  $90^\circ$  (hydrophilic).

The results of scanning electron microscopy can be seen in figure 7, that in two nanostructures there is presence of hexagonal geometries, powders and nanowires; for the case of the film on the surface, small spheres on a homogeneous layer are noticed.



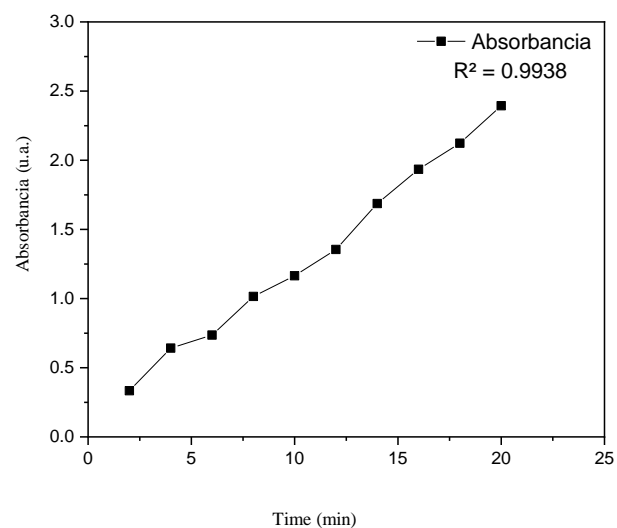
**Figure 7** Scanning electron microscopy of zinc oxide nanostructures. a) powders, b) thin film and c) nanowires

The photocatalytic tests used aliquots starting from a 20ppm stock solution. It was diluted to 10 points per 10%. As shown in figure 8, the concentration changed colour as the percentage decreased.



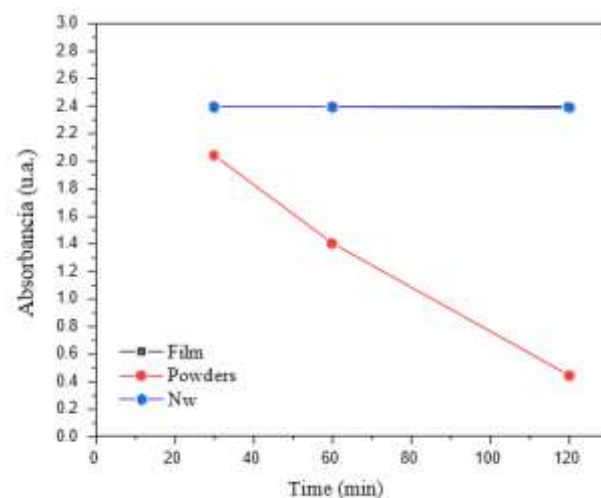
**Figure 8** Aliquots taken for the calibration curve

Once the dilutions were available, they were taken to a spectrophotometer to measure the absorbance and generate the calibration curve presented in graph 1. The linear correlation coefficient the linear correlation coefficient shows a value of 0.9938, which indicates a low variation of the data following a linear trend.



**Graph 1** Calibration curve of methyl orange (MN)

Graph 2 shows the degradation of methyl orange (MN) with respect to the different ZnO nanostructures exposed to irradiation under ultraviolet light.



**Graph 2** Degradation of methyl orange with respect to time

The nanowires and zinc oxide films show a poor degradation of methyl orange compared to nanostructured ZnO powders.

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## 6. Conclusions

The results obtained on the photocatalytic performance of the 3 types of nanostructures show a higher performance for the zinc oxide nanopowders, being that degradations were obtained from the thin films and nanowires, while they do not present photocatalytic activity. The degradation rate of methyl orange with the zinc oxide powders increased with time.

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