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Graphical abstract

Synthesis and characterization of 1D metal oxide nanostructures: Titanium dioxide nanotubes (TNTs) and Zinc oxide nanobars (ZNBs)

Abstract

The objective of this work consisted about the synthesis and characterization of 1D metal oxide nanostructures. For that, titanium dioxide nanotubes (TNTs) were synthesized with uniform size distribution through the hydrothermal method. Also, individual zinc oxide nanobars (ZNBs) without growing substrate and with uniform size distribution were obtained by same method and by wet chemical reaction. These nanostructures were characterized using Electron Diffraction (ED), Scanning Electron Microscopy (SEM) and

Keywords

Nanostructure
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Nanotubes
Nanobars

Transmission Electron Microscopy (TEM). ED analysis showed that nanotubes and nanobars were effectively of anatase titanium dioxide (TiO_2) and wurzite zinc oxide (ZnO) respectively, with preferential growth in the direction [100]. In the same way, SEM and TEM analysis revealed a nanotube and nanobar morphology for TiO_2 and ZnO nanostructure respectively. These were catalogued like quantum thread (two dimensions in nanoscale), where TNTs had an average diameter of 11.35 nm and an average length of 176.97 nm, presenting a narrow size distribution. On the other hands, ZNBs had an average of 156.00 nm and an average of 4.98 micrometers, presenting a wide distribution of sizes. In both cases, a conversion of more than approximately 95 % is obtained.

Síntesis y caracterización de nanoestructuras de óxidos metálicos en 1D: Nanotubos de dióxido de titanio (TNTs) y nanobarras de óxido de zinc (ZNBs)

Resumen

El objetivo de este trabajo consistió en la síntesis y caracterización de nanoestructuras de óxido metálico en 1D. Para esto, se sintetizaron nanotubos de dióxido de titanio (TNTs) con distribución de tamaños uniforme a través del método hidrotermal. También se obtuvieron nanobarras individuales de óxido de zinc (ZNBs) sin sustrato de crecimiento y con distribución de tamaños uniforme mediante el mismo método y por reacción química húmeda. Estas nanoestructuras se caracterizaron mediante Difracción Electrónica (ED), Microscopía Electrónica de Barrido (SEM) y Microscopía Electrónica de Transmisión (TEM). El análisis de DE mostró que los nanotubos y las nanobarras eran efectivamente de anatasa dióxido de titanio (TiO_2) y óxido de zinc wurzita (ZnO) respectivamente, con un crecimiento preferencial en la dirección [100]. Del mismo modo, el análisis SEM y TEM reveló una morfología de nanotubos y nanobarras para las nanoestructuras de TiO_2 y ZnO , respectivamente. Estos se catalogaron como hilos cuánticos (dos dimensiones en nanoescala), donde los TNTs tenían un diámetro promedio de 11.35 nm y una longitud promedio de 176.97 nm, presentando una distribución de tamaño estrecha. Por otro lado, las ZNBs tenían un promedio de 156.00 nm y un promedio de 4.98 micrómetros, presentando una amplia distribución de tamaños. En ambos casos, se obtuvo una conversión de más del 95 % aproximadamente.

Palabras clave

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Synthesis and characterization of 1D metal oxide nanostructures: Titanium dioxide nanotubes (TNTs) and Zinc oxide nanobars (ZNBs)

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The objective of this work consisted about the synthesis and characterization of 1D metal oxide nanostructures. For that, titanium dioxide nanotubes (TNTs) were synthesized with uniform size distribution through the hydrothermal method. Also, individual zinc oxide nanobars (ZNBs) without growing substrate and with uniform size distribution were obtained by same method and by wet chemical reaction. These nanostructures were characterized using Electron Diffraction (ED), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). ED analysis showed that nanotubes and nanobars were effectively of anatase titanium dioxide (TiO₂) and wurzite zinc oxide (ZnO) respectively, with preferential growth in the direction [100]. In the same way, SEM and TEM analysis revealed a nanotube and nanobar morphology for TiO₂ and ZnO nanostructure respectively. These were catalogued like quantum thread (two dimensions in nanoscale), where TNTs had an average diameter of 11.35 nm and an average length of 176.97 nm, presenting a narrow size distribution. On the other hands, ZNBs had an average of 156.00 nm and an average of 4.98 micrometers, presenting a wide distribution of sizes. In both cases, a conversion of more than approximately 95 % is obtained.

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1. Introduction

Nanotechnology is a broad branch that covers the study, design, creation, synthesis, manipulation and applications of materials, devices and functional systems through the control of matter at the nanoscale, and the exploitation of phenomena and properties of matter at these sizes. It is worth mentioning that the nanoscale or nanoscale is described by values of 10⁻⁹ m [1]. In this research

the term nanotechnology is used in the broad sense, which encompasses a number of disciplines. At present, two types or paths of nanotechnological development are generally distinguished, the top-down path and the bottom-up path (Bottom-up) [1, 2].

In addition, there are several ways to classify nanostructures; the most usual is considering the number of directions in which the particles or carriers can move freely. There are quasi-two-

dimensional quantum wells, quasi-one-dimensional or cylindrical quantum strands, and quasi-zero-dimensional or spherical quantum dots [3]. This type of classification is observed in Figure 1.

According to this way of determining the type of nanostructures, Nanoparticles (NPs) stand out as a quasi-zero-dimensional quantum system, since all their dimensions are below 100 nm. While the Nanobars (NBs) and Nanotubes (NTs) correspond to a quasi-one-dimensional quantum system, since they have a length in which the particles or carriers can move freely. It should be noted that NTs are formed by nanolamines that have two directions for free movement. In this way, the quantum threads have a very small diameter, and that is why electrons experience quantum confinement in the transverse direction. The quantum effects present in this type of structure affect the properties of transport (thermal conductivity, viscosity, electrical conduction and diffusion). Due to the confinement of electrons, its transverse energy is quantized in a series of discrete values. So the electrical and optical properties are different thanks to these confinements. These changes do not occur only in quantum threads, but also in the other systems mentioned above. Next, the compounds and nanostructures used will be described, which have a great relationship with regard to electrical and optical properties specifically [4].

1.1 Titanium oxides

Titanium is a transition metal widely found in the earth's crust. This element and like many others, is not in a pure state, as most tend to react and join other elements. Ti is not the exception and is found in several types of compounds, mainly forming part of minerals such as anatase, brookite, ilmenite, perovskite, rutile, titanite, as well as being present in many iron minerals [5].

The scientific and study interest in this material falls on compounds in which oxygen is the only element bound to Ti, that is, in Ti oxides. Of all the compounds that this metal forms, only anatase, brookite and rutile are compounds that fulfill this quality [6].

Although the three minerals have the same chemical formula (TiO_2) and visually form a white powder, their structural and optical properties are different, but with similarities. Among the three types of titanium dioxide the most abundant and

Figure 1. Quantum systems a) Quantum well (2D), b) quantum thread (1D) and c) quantum dot (0D) [3].

Figure 2. Crystal structures a) Rutile, b) brookite and c) anatase [9].

studied is the rutile with a bandwidth of 3.0 eV and tetragonal crystalline structure. Anatase is the most used phase in laboratory studies including this research and also the least abundant, with a bandwidth of 3.2 eV and tetragonal crystal structure, while brookite is the least known with a bandwidth of 3.2 eV and an orthorhombic structure [6-9], (as shown in Figure 2).

Most applications have been studied and manufactured in powder form. In this study the anatase phase was used, since this form seems to be more attractive than rutile and brookite in a wide range of applications including: catalysis, photocatalysis, solar energy conversion, protection surface coating, ceramic, pigments, in the field of biology, the food industry, as a reducer in corrosion among others [10]. One of the most peculiar properties of anatase, along with other nanometer-scale materials, is the ability to improve the mechanical properties of polymer matrix nanocomposites, by acting as reinforcement in small quantities [11].

1.1.1 Titanium dioxide nanotubes (TNTs)

The different titanium dioxide nanostructures that are obtained (see Figure 3) are NWs, NBs, NPs,

Figure 3. Different nanostructures of TiO_2 . a) NCs, b) NBs, c) NTs, d) NPs and e) NWs.

Figure 4. Crystal structures ZnO . a) Hexagonal wurtzite [26], b) Cubic rock salt and c) Cubic zinc blende [25].

NTs, [12, 13] where the great attraction of this metal oxide lies in the fact that these structures have excellent electronic and electrical properties, optical and chemical [14].

The manufacture of these nanostructures has been developed especially via three processes, which have undergone variations with the aim of producing a number of new materials with several promising applications. The most common methods of obtaining punctually for nanotubes are titanium dioxide, electrochemical anodic oxidation [15], sol-gel method [16] and the hydrothermal method [17]. This last one is of great importance for this investigation since this method has the particularity of being a simple way to obtain tubular morphologies and with a great performance.

The TNTs get a lot of attention due to their tubular structure, which increases the functionality of titanium dioxide (simple particles) in many applications. The large surface area provided by the walls (interior and exterior) of the nanotubes and their porosity increases the surface area, increasing the effectiveness in catalysis, energy storage (photocatalysis), coatings among others [18].

1.2 Zinc oxides

Zinc is a bluish-white material, which, like titanium, is found in the earth's crust, accompanied by other chemical elements, forming different types of compounds such as zincite, five-chromite, hydrozincite, wurtzite, among many others [19]. Zinc oxide is a white chemical compound which can crystallize in three different ways; Wurtzite, hexagonal packing, salt rock type and zinc cube both cubic [20] (See Figure 4).

This oxide has a bandwidth of 3.37 eV and high excitonic bond energy of 60 meV at room temperature [21]. The difference in electronegativity between zinc and oxygen produces a high degree of ionicity in its bond. This material has attracted great interest because of its interesting physical properties, highlighting its excellent optical and electrical properties [22]. Furthermore, cataloged as a key technological material due to the lack of a center of symmetry in the ZnO type Wurtzite hexagonal (Figure 4a), combined with the

Figure 5. ZnO nanostructures. a) NPs, b) NEs, c) NAs and NWs, d) NAs, e) NCs, f) NBs, g) NSs, h) NWs, ei) NTs.

large electromechanical coupling, results in strong piezoelectric, pyroelectric, optical and electrical properties [23], resulting in multiple applications such as electromechanics, piezoelectric sensors, field emission screens, solar cells and gas sensors [24, 25]. ZnO can replace TiO_2 in some applications due to its similarity in its physical and chemical properties. Reason why these two types of materials have been selected for the study.

1.2.1 Zinc oxide nanobars (ZNBs)

The oxide of zinc presents the majority of the configurations of nanostructures that a material can

form; NWs, NCs, NBs, NTs, nanostars (NSs), nanorings (NAs), nanospirals (NEs), etc. [26] This material has interesting properties in low dimensional structures. In the nanometric size range, ZnO is expected to present interesting physical properties and a deep coupling effect compared to micrometer material (see figure 5) [27].

There are several ways to synthesize ZnO nanostructures, such as by evaporation and thermal condensation, deposition in aqueous solution, chemical vapor organic organometallic deposition (MOCVD) and molecular beam laser epitaxy (MOVPE) [28]. These techniques have been used

in the manufacture of ZnO nanostructures including NBs, NWs, NSs, NCs, NTs and quantum dots (in Figure 5 different ZnO nanostructures are observed). In the above processes, high temperature and very long growth times are usually required, only the method of deposition in aqueous solution allows the growth at low temperature of the nanostructures, but these have a large number of defects [25]. The properties of each of the nanostructures vary depending on the synthesis technique used [29].

ZnO semiconductor nanobars have unique chemical and physical properties and thanks to this type of nanostructures it is possible to develop nanodevices such as: ultraviolet photodetectors, gas sensors, field effect transistors, optoelectronics, Schottky diodes and light emitting devices [30-32]. This is why this research tries to contribute to the development of new nanomaterials and nanocomposites. Therefore, the synthesis of TNTs and ZNBs was carried out, with potential applications as reinforcements for epoxy resin matrices. These nanocomposites have a high development potential due to all the new properties and applications they offer.

2. Experimental section

2.1. Synthesis of TNTs

As mentioned above, a method was used for the massive preparation of TNTs by means of hydrothermal synthesis in which a transformation yields close to 95 % was sought. The scheme of the synthesis is summarized in Figure 6.

2.1.1 Synthesis of nanotubes of titanium dioxide via hydrothermal treatment

In the reactions TiO_2 anatase phase and NaOH were used, all acquired in Sigma Aldrich and were of analytical quality. For the synthesis, the following procedure was carried out: 0.15 g of TiO_2 were mixed with 14 mL of an aqueous solution of 10 M NaOH, and then treated in a hydrothermal process at 150°C in a stainless steel autoclave with a container Teflon inert with a capacity of 23 mL, it supports a maximum temperature of 250°C with a pressure of 12.41 MPa for 48 hours, the reactor was acquired at the Parr instrument company. After the reaction was

completed, it was washed and filtered with distilled water. Then the solution was dried in a heating oven with controlled temperature at 80°C for 10 hours. To remove the high content of NaOH more thoroughly, it was washed magnetically stirring repeatedly with distilled water and ultrasound (30 seconds), then the liquid was separated by means of centrifugation. This process was repeated 6 times. Then, particle agglomerated nanotubes were added to a solution of distilled water with ethanol in a 1:1 ratio and stirred for 6 hours before being dried again at 80°C in the oven for 10 hours.

2.2 Synthesis of ZNBs

Two different methods of massive synthesis of ZNBs were investigated to obtain a yield close to 100 % and a uniform size of said nanobars. The methods used were hydrothermal synthesis (the aforementioned autoclave was used) and chemical reaction via wet (a glass reactor vessel was used), in both concentrations, time and temperature were varied. The overall process is observed in Figure 7.

2.1.2 Synthesis of zinc oxide nanobars via hydrothermal treatment and chemical reaction via humid

In the reactions, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$) and NaOH as a reducing agent were used, acquired in Sigma Aldrich and with analytical quality. For the reaction, $\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and NaOH were added, to be then treated in a hydrothermal process in a 23 mL capacity autoclave and by wet chemical reaction in a glass reactor vessel with a capacity of 300 mL. The temperature used was 70°C and 80°C .

Figure 6. Scheme manufacturing of TNTs.

Figure 7. Scheme manufacturing of ZNBs.

Table 1. Synthesis conditions by the hydrothermal method and wet chemical reaction.

Technique	Reagent concentration NaOH/ Zn(NO ₃) ₂	Time (h)
Hydrothermal (Autoclave 23 mL)	1/1	4
		8
		12
	4/1	4
		8
		12
Wet way (Reactor of 300 mL)	4/1	12
	40/1	20

A summary of the parameters that were varied in the treatments is described in Table 1. The technique, the concentration of the reactants, the temperature, the reactor and the time were varied, and then it was washed with distilled water and dried in a heating oven at 80 °C for 10 hours.

2.3 Characterization of nanostructures

The characterization of the morphology of the TNTs and the ZNBs were determined by scanning electron microscopy (SEM) using the JEOL JSM-6380LV equipment of the Spectroscopy and Microscopy Center (CESMI) belonging to University of Concepción. For the analysis in the SEM a small drop was placed on a carbon tape, adhered to an aluminum sample holder then this sample was coated with a nanometric layer of gold to give conductivity to the surface and increase the resolution of the image, obtaining more contrast

and preventing the sample from being charged electrostatically.

The characterization of the particle size and the electron diffraction patterns were obtained by transmission electron microscopy (TEM) using the JEOL-JEM 1200 EXII equipment from CESMI. For the analysis in the TEM, a drop was placed in a copper grid (150 mesh) covered with a carbon film, later the grid was dried in a light source for its visualization.

The digitalization and edition of the images obtained by means of SEM and TEM was carried out using the Gatan Digital Micrograph™ software version 3.7.0.29 distributed by Gatan (Pleasanton, CA, USA). The analysis of electron diffraction patterns was achieved using the software CaRIne 3.1 Crystallography (Divergent S.A, France).

3. Results and discussion

3.1 Synthesis of nanostructures

3.1.1 Synthesis of TNTs by hydrothermal method and its characterization

Synthesis of TNTs was carried out by hydrothermal method in the presence of a highly concentrated NaOH solution. The high concentration of OH⁻ ions allows the formation of sheets of titanates which are stabilized by the Na⁺ counter ion. When the resulting material is washed after the growth process, the final pH of the solution is close to 7, so that the counter ion is removed and the folding of the nanotubes occurs. This leads to the formation of multilayer pipes. Controlling the process for obtaining tubes with a single wall is extremely difficult using this growth technique, so it is generally not used for these purposes. The reaction has a conversion percentage greater than 90 %, that is, generally all the material that is produced corresponds to nanotubes. One of the problems presented in the synthesis was due to the agglomeration of the tubes before and after the washing process, this can be seen in Figure 8. The agglomeration is due to the interaction of titanates with each other, so it is probable that at the moment of the folding of the sheets they become entangled between them. Another possible reason is due to these tubes are long which, at the time of washing and concentration by centrifugation, to

Figure 8. a) SEM image of TNTs obtained by the hydrothermal method, the agglomeration of the tubes is observed after the washing process, b) TEM image, as in the SEM, clusters of TNTs are evident in the whole agglomerated nanotube grid.

Figure 9. a) and b) SEM images of TNTs after the washing process with magnetic stirring and sonication. c) TEM image of TNTs with d) their respective diffraction pattern. The indexation verifies that the material corresponds to TiO_2 (Anatase). e) and f) micrograph where the dimensions and thicknesses of the nanotubes are observed. f) the walls of the tubes are observed.

remove the liquid provided with NaOH and other residues of the reaction, become entangled with each other agglomerating, similar results have been reported by Xuejun Zou et al [33].

To avoid the agglomeration of the nanotubes, we proceeded to wash with magnetic stirring for 30 minutes, sonification and subsequent centrifugation. Sonification was not prolonged for a long time since this can cause tube rupture [34,35]. The washing treatment helps to eliminate more efficiently the impurities (sodium ions and reaction residues) so that more compact nanotubes are obtained. The results of the previous process can be found in Figure 9 a) and b). These images of SEM show the large amount of synthesized nanometric material, which proves that hydrothermal synthesis is an efficient process for obtaining TiO₂ with a conversion percentage higher than 99 %. It should be noted that the reaction time is important in this synthesis since an insufficient time can lead to an incomplete conversion, obtaining in this way nanotubes mixed with nanoparticles [35]. The indexation of the diffraction pattern (Figure 9d) determined the following distance $d(h, k, l) = 3.54$, $d(h, k, l) = 2.38$, $d(h, k, l) = 1.92$ Å and $d(h, k, l) = 1.67$ Å, corresponding to planes (101), (103), (200) and (105) respectively. These spacings were compared with the unit cell of anatase TiO₂ using the CaRine Crystallographic program (Cyrille Boudias & Daniel Monceau-WANADOO) and the file with code 01-0562 obtaining an error lower than 5 %. Concluding that the NTs of TiO₂ are anatase phase. On the other hand, in Figures 8 a) and b) gives the impression that the TiO₂ have a diameter that is on the micrometer scale, which is discarded in Figures 9 c) and d), because they remain attached but not forming aggregates. In the preparation of the samples for TEM the NTs are dispersed homogeneously and then a micro drop is placed on top of the grid. This is the reason why they are observed separately. It is highlighted and clarified that the images of SEM are made in solid state for this reason "agglomerated" nanotubes are observed. In the spectrum of the image in f) a thickness of 14 nm is observed in the scan line of a nanotube highlighted by a box. The shape of the spectrum between the black lines rules out that the nanostructures analyzed are nanowires since in the center of this range there is a pronounced pick characteristic of tubes and not wires. If this

spectrum is compared with that of the image in Figure 15, the previous comment is checked. Obtaining the diameter of the tubes from Figure 9 e) and f), is inaccurate since the lines of tracing in the spectrum of the diameters of the tubes is difficult to adjust. However, a deeper exploration by means of high-resolution TEM microscopy can confirm the diameter of the tubes more accurately. Thus, by randomly selecting a number of tubes, their respective diameters were determined, the data obtained were plotted in a relative frequency histogram versus the thickness using the origin 8.0 program (origin lab corporation ®). The results are in Figure 10.

The normal curve of Figure 10a indicates that the average diameter of the NTs obtained is 11.16 nm (sd 0.1203, area 0.40), while the average length (Figure 10 b) was 177.27 nm (sd 0.279, area 0.112). Other works such as that of Lain-Chuen *et al* [36], report diameters between 12 nm - 37 nm and lengths between 100 nm - 300 nm. As in this work, the nanotubes were synthesized by the hydrothermal method using another type of autoclave. It should be noted that the diameter and the filling of the reactor are preponderant in the synthesis since the pressure of the system is very sensitive to these parameters. On the other hand, Tacchini *et al.* [37], obtained diameters between 7-10 nm, while Méndez-Cruz *et al.* [38] obtained diameters similar to those reported in this work but with a wide distribution 11-18 nm. A more detailed analysis was performed by means of high resolution TEM (Figure 11), images a) and b) correspond to measurements of the walls of the tubes to determine the arrangement and direction of growth of the walls.

Figure 10. Distribution of external diameter sizes a) and long b) of the TNTs obtained via hydrothermal.

Figure 11. a) and b) High resolution TEM images of the walls of the TNTs. Both images show the processing by means of FFTs and filtering, being able to obtain the respective interplanar distances and the direction of growth of the walls of the tubes. c) Determination of the internal and external diameters of the nanotubes.

The analysis was performed using the Digital Micrograph (DM) 3.7.0 program from "Gatan Inc". Initially the image processing begins with the application of FFTs (Fast Fourier Transform), and then, FFTs results in points separated from a center as well as a diffraction pattern (PD). Therefore, this image contains information related to the space between planes so it can be used as a PD. To filter the image, we proceed to use a mask where the points of the FFTs image are selected, obtaining in this way a clean image as shown in figures a) and b).

The planes obtained are perpendicular to the line joining each FFTs, then the spacing of the planes was measured and it was found that the walls of the TNTs are addressed in [100] which was evidenced by a distance of 1,875 Angstroms. It is important to note that the image in Figure 11a does not present planes in the same direction but in [111] with an interplanar distance of 2.13 Angstroms. It is possible that the intensity of the electron beam of the equipment degrade in a certain proportion the walls of the tubes producing particles of TiO_2 ; This can be verified by observing the images in detail, they can appreciate particles forming the walls of the tube.

On the other hand, in the image of Figure 11c, the walls of the tubes are shown more clearly, internal diameters of 4.0 nm and widths of 1.5 nm, respectively, were obtained. So, the full diameter of the nanotube would be 7 nm, which does not agree with what is analyzed in the frequency diagrams. These differences are due to the exposure of the sample to the high resolution TEM electron beam which works up to 200 KV. For TNTs synthesized by means of the hydrothermal method, internal diameters of 5 nm are reported [37], other similar works obtain internal diameters between 5 to 15 nm [38], with diameters of the walls between 0.5 nm and 0.7 nm [39,40]. The differences of this work between those reported may be due to the time to a synthesis with higher system pressure allowing larger walls and even larger internal diameters. The formation of the TNTs is currently under discussion and the authors do not agree on whether the structure of these is periodic or not [41], the discussion is focused on the synthesis process especially via hydrothermal because it is uses a very high amount of NaOH (very basic pH).

Therefore, the composition of the tubes can vary and can even be made up of parts of TiO_2 or titana-

Figure 12. a) Projection (010) of the unit cell of $H_2Ti_3O_7$, b) model of the structure of the nanotubes assuming that the composition of the sample corresponds to $H_2Ti_3O_7$ and c) proposed by Chen et al.

tes of different formulas such as $H_2Ti_3O_7$ (Figure 12). However, the consensus is that the growth direction is the same for all configurations of TNTs and is address [100]. This direction is in accordance with the results presented above since the TNTs synthesized in this work have the same growth direction. Due to this it is concluded that these TNTs are arranged in the zone axis (010) of the microscope which makes them aligned and that direction can be evidenced as shown in Figure 12b. Each reaction mentioned in the previous chapter resulted in 0.1 g of TNTs, calculated after finishing all the washing, dispersing and drying processes.

3.1.2 Synthesis of ZNBs by hydrothermal and wet chemical reaction method and its characterization

The experiments related to this synthesis are shown in Table 1. Initially it was used of stainless steel autoclaves, the same ones that were used in the synthesis of TNTs. Initially is showed the results where the same ratio of precursors (1:1) and different reaction times; 4, 8 and 12 hours, respectively. The images of Figure 13 correspond to the results of the mentioned treatments. Figures 13 a) and c), are a reaction time of 4 hours. It is observed that neither particles or rods were formed but on the contrary a kind of polycrystalline film

Figure 13. a), c) and b), d) TEM images and diffraction pattern of the materials obtained by means of hydrothermal synthesis with the same proportion of reactants at 4 hours of treatment (1:1). e), g) and f), h) diffraction images and patterns of the materials obtained at 8 and 12 hours, respectively. (Results corresponding to experiments by hydrothermal method).

was formed, this was concluded by the diffraction pattern shown in Figures 13 b) and d). Monolayer diffraction patterns give points with defined lines indicating an order with some preferential growth [42]. These types of leaves have been obtained by Yuan-Chang [43] through wet methods.

There may be two factors so that these sheets or sheets are obtained and not NBs, this may be due to the low amount of OH^- ions in solution, since the competition of different growth reactions is possible, therefore the growth for the Leaf

production is facilitated with low amount of OH⁻ and low reaction times [44]. In the diffraction patterns, the interplanar distance ($d(hkl)$) of 2.60 corresponding to the planes (002) of the hexagonal wurtzite type ZnO [45] was determined. On the other hand, the increase of the reaction time at 8 and 12 hours did not produce significant results in the synthesis; this is shown in the Figures 13 e) and g), where particles and aggregates (micro-stars) were obtained, respectively. The analysis of the diffraction patterns concluded that, like the previous experiments, the material obtained was ZnO.

On the other hand, the results of the treatments are analyzed, increasing the proportion of NaOH in relation to Zn(NO₃)₂ 4 times. Using the same amount of reactive solution and the same reaction times 4, 8 and 12 hours. The images of these results are shown in Figure 14. Observing the TEM micrographs, the same results as those obtained in the previous experiments are observed. That is, the parameters used in the synthesis do not produce the NBs that are desired for the production of nanocomposites. In this treatment, larger ZnO nanoparticles were obtained at 8 hours and aggregates (stars) at 12 hours.

According to the previous results, it is evident that both the reaction time and the variation of the ratio of synthesis precursors do not produce NBs, but on the contrary, different ZnO nanostructures. The most approximate case for both are the treatments at 12 hours, the structures obtained in this reaction time suggest that the increase in time is important in obtaining the ZNBs. The diffraction patterns confirmed that the material is ZnO hexagonal wurtzite type.

Due to the above results it was determined to change the hydrothermal system using the autoclave by a low-pressure hydrothermal system using a glass reactor with a higher capacity. It is probable that the increase in pressure in the autoclave is unfavorable for the formation of the NBs and as mentioned in the case of the synthesis of TNTs the hydrothermal synthesis is very sensitive to changes in pressure which is dominated by the size of the reactor, the filling of this and also by the reaction time. In the wet chemical reaction experiments, 300 mL of solution was used to effect growth, the amounts of reactant solutions were the same for both reagents (150 mL).

Figure 14. a), c), e) and b), d), f) TEM images and diffraction patterns of the materials obtained by means of hydrothermal synthesis with different proportions of reactants (4: 1 of NaOH and Zn(NO₃)₂) a different treatment times 4, 8 and 12 hours, respectively of treatment. (Results corresponding to the experiments via chemical wet reaction).

In the first case, no change was noticed; the same stars were obtained, concluding that the reactor did not affect the results. Subsequently, the reaction time was increased to 20 hours using a ratio 40:1 of precursors. The results of these treatments are shown in Figure 15, 16 and 17, respectively. For the ratio 1:40 the formation of NBs with a size located in the micrometric scale was evidenced. The TEM image of Figure 15. It indicates that these are thick since it is difficult for the electron beam to cross them, giving rise to a dark image in the center. The diameter of these NBs ranges from approximately 120 nm to 400 nm with lengths exceeding 16 microns. The thickness spectrum of this image shows the wide distribution in the diameter of the bars and it is also shown in the consecutive spectrum that they are not pipes because the concentric pick between each diameter is not observed, as was the case with TNTs.

By making an overlay of images such as those shown in Figure 16, it can be seen that the cluster of bars have a concentric origin where they begin to grow. Due to its thickness this could not be observed in Figure 15. Therefore, the length of these is determined from the center of growth. The lengths then vary between 4 and 12 microns, diameters below 100 nm are also evident. Alike results were reported by Khramovskyy et al [46] as

Figure 15. TEM image of ZnO microbars obtained at 20 hours by hydrothermal treatment at low pressure.

Figure 16. a) Superposition of three TEM images of ZnO microbars obtained at 20 hours by hydrothermal treatment at low pressure. b), c) and d) superimposed images. With the respective analysis of spectra of size and length.

well as by many other researchers.

On the other hand, to analyze the growth center of ZnO bars, an MEBT analysis (better known as STEM) was carried out. Initially, a TEM analysis was performed (Figure 17a) and a sweep was carried out on that area (Figure 17b). A center of growth of the bars was evidenced where they grow between 6 and 20 points, which have a hexagonal shape proper as it is characteristic of the wurtzite ZnO.

The conglomerates are shaped like flowers (Figure 17c) which open up as the diameter of the bars grows, so the high pressure of the center part, obtaining shapes like the one shown in Figure 17 d). In the EDS spectrum picks corresponding to the

signals of [Zn (L), Zn (K)] and [O (K)] are shown, this verifies that the bars are effectively formed of ZnO.

3.1.3 Analysis of the Size of the ZnO Nanobars

The size analyzes were determined using Figure 18. In part a) of the first image, the formation of NBs is shown because the width of these oscillates between 10 nm and approximately 410 nm, with the greatest tendency being around 50 to 90 nm with an average of 156 nm. On the other hand, the length exceeds the nanometer barrier, reaching 12 micrometers. The greater tendency indicates the formation of NBs of a length that oscillates between the 4 and the 6 micrometers predominantly; the average was of 4.98 micrometers.

In b) the difference in size between the NBs, from some of a few nanometers to others of dozens of them is showed. In c) a large nanobarra with a diameter of 120 nm d) and a length of 3 micrometers e) is observed, showing that this nanostructure is not hollow. Finally, the patterns DE in f) and those found in the previous images were studied.

Figure 17. a) TEM image and diffraction pattern of ZnO bars, b), c) STEM image of ZnO bars, d) EDS spectrum and STEM mapping ZnO bars obtained by the hydrothermal method at low pressure with a reaction time of 20 hours.

Figure 18. ZnO TEM micrographs, a) dispersed nanobars TEM, b) nanobars of different TEM sizes, c) nanobars on color scale "temperature" TEM, d) nanobar individualized TEM, e) width and f) length of the nanobars TEM, g) DE.

The values of the calculated distances agree with the values corresponding to hexagonal ZnO, $d(h, k, l) = 2,869$ Å associated to the plane (100) (which is the plane of growth of the crystal), $d(h, k, l) = 2,502$ Å associated to the plane (101), $d(h, k, l) = 1,974$ Å associated to the plane (102), $d(h, k, l) = 1,682$ Å associated to the plane (110), $d(h, k, l) = 1,481$ Å associated to the plane (103) and $d(h, k, l) = 1,381$ Å associated to the plane (201), all the available previous data were compared with the theoretical diffraction patterns of the hexagonal ZnO of the program CaRIne 3.1, and with the code 01-1136 obtaining an error lower than 5 % in the latter.

4. Conclusions

It was determined that the hydrothermal method is effective in the production of TNTs with narrow size distribution both in the width and in the length of the nanostructure. Agitation in a 1:1 solution of distilled water with ethanol was key in the dispersion and formation of short TNTs, maintaining the tubular shape. It was determined by DE that the TNTs were TiO_2 phase anatase (tetragonal).

Also, a procedure was established for the massive synthesis of ZNBs by means of a chemical reaction via the wet, without the contribution of a substrate that initiates growth. Obtaining ZNBs with a wide

distribution of sizes (length and width) and sizes that are mostly in the micrometric scale and have the same birth center where they grow from 6 to 20 points. It was determined by DE that the ZNBs were ZnO wurtzite (hexagonal).

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Conflicts of interest

The authors declare that they have no conflicts of interest of any kind in relation to the publication.

Acronyms

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
ED	Electron Diffraction
NBs	Nanobars
NPs	Nanoparticles
NFs	Nanofibers
NWs	Nanowires
NTs	Nanotubes
MOCVD	Chemical vapor organic organo-metallic deposition
MOVPE	Molecular beam laser epitaxy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TNTs	Titanium dioxide nanotubes
ZNBs	Zinc oxide nanobars
ZNPs	Zinc oxide nanoparticles

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