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MANUFACTURING OF ZNO SEMICONDUCTORS FROM THE ZN(CH3COO)2•2H2O PRECURSOR VIA A POLYOL-MEDIATED THERMOLYSIS PROCESS

FABRICACIÓN DE SEMICONDUCTORES DE ZNO A PARTIR DEL PRECURSOR ZN(CH3COO)2-2H2O MEDIANTE UN PROCESO DE TERMÓLISIS MEDIADO POR POLIOL

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Manufacturing of ZnO semiconductors from the $Zn(CH_3COO)_2•2H_2O$ precursor via a Polyol-Mediated Thermolysis Process

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ABSTRACT

In this work, the instrumentation of a system to manufacture ZnO semiconductors using the Polyol-Mediated Thermolysis Process are reported. The semiconductors manufactured from the $Zn(CH_3COO)_2•2H_2O$ precursor have been synthesized in different molar concentrations (0.001 M, 0.01 M, and 0.1 M), at low temperatures and atmospheric pressure. The structural and morphological characteristics of the ZnO semiconductors were studied by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD has been confirmed the manufacturing of the ZnO semiconductors with high crystalline quality. No other crystalline phases were detected. The SEM micrographs reveal that the morphology of the non-agglomerated quasi-spherical particles (composed of nanometer-sized particles) has been controlled from the agglomerated particles, when the concentration of 0.001 M to 0.01 M is used, respectively. When the highest concentration has been used, no aggregation occurs and only tiny particles in the nanosized range are obtained. As a result, the synthesis route successfully demonstrates the manufacturing of semiconductors in a single step, in a simple-strategy process, being of low cost and scalable to industrial level.

Keywords: polyol-mediated thermolysis process, scalable zno production, structural and morphological characterization

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Fabricación de semiconductores de ZnO a partir del precursor Zn(CH3COO)2-2H2O mediante un proceso de termólisis mediado por poliol

RESUMEN

En este trabajo se presenta la instrumentación de un sistema de fabricación de semiconductores de ZnO mediante el proceso de termólisis mediada por poliol. Los semiconductores fabricados a partir del precursor Zn(CH3COO)2-2H2O se han sintetizado en diferentes concentraciones molares (0.001 M, 0.01 M, y 0.1 M), a bajas temperaturas y presión atmosférica. Las características estructurales y morfológicas de los semiconductores de ZnO se estudiaron mediante difracción de rayos X (DRX) y microscopía electrónica de barrido (SEM). La DRX ha confirmado la fabricación de los semiconductores de ZnO con alta calidad cristalina. No se detectaron otras fases cristalinas. Las micrografías SEM revelan que la morfología de las partículas cuasi esféricas no aglomeradas (compuestas de partículas de tamaño nanométrico) se ha controlado a partir de las partículas aglomeradas, cuando se ha utilizado la concentración de 0,001 M a 0,01 M, respectivamente. Cuando se ha utilizado la concentración más alta, no se produce agregación y sólo se obtienen partículas diminutas en el rango de tamaño nanométrico. Como resultado, la ruta de síntesis demuestra con éxito la fabricación de semiconductores en un solo paso, en un proceso de estrategia simple, siendo de bajo coste y escalable a nivel industrial.

Palabras clave: proceso de termólisis mediado por poliol, producción escalable de zno, caracterización estructural y morfológica

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INTRODUCTION

Zinc Oxide (ZnO) is a II-VI type-N semiconductor compound with a band gap around 3.37 eV and a wurtzite-type crystalline structure as a stable phase at room temperature. It has specific optical, electrical and thermal properties that are very important for a wide range of applications, especially in the field of the electronic and optoelectronic. However, currently the interest main focus, both scientific and technological, has been directed towards obtaining nanostructured materials due to the superior properties they show compared to bulk materials, promoting the development of various techniques that allow the obtaining of ultrafine particles (Ramos-Justicia, et al., 2023).

Due to the different properties and potential applications of ZnO, the renewed interest in nanostructured ZnO particles has been driven by their attractive and improved properties (electrical, optical, magnetic and mechanical), for applications including nanolasers, ferromagnetic semiconductor nanomaterials, piezoelectric semiconductors, among other (Ramos-Justicia, et al., 2023; Salvador Alcántara, et al., 2008). Recently, the physical and chemical properties of nanostructured ZnO also make it very attractive for wastewater treatment, attracting considerable attention due to its photocatalytic property for the degradation of various environmental pollutants (Flores-Carrasco et al., 2014; Muñoz-Fernandez et al., 2017; Flores-Carrasco et al., 2021,).

The results discussed above suggest that there are still several problems to be solved for devices based on ZnO nano- and microstructures to reach optimal efficiencies and be truly competitive within the technological market. Among the fundamental problems is the control of the morphological and structural properties of the ZnO nano- and microstructures in relation to their manufacturing process. Therefore, the great technological interest aroused by the ZnO and the existence of points open to study and improvement in its manufacturing processes, have been driven the development and interest in the generation of different synthesis methodologies. Up till now, the synthesis methods such as: spray pyrolysis (Salvador Alcántara, et al., 2008; Flores-Carrasco et al., 2014), hydrothermal (Sierra-Fernandez et al., 2014), solvothermal (Muñoz-Fernandez et al., 2017), vapor-solid (Bueno et al., 2018, Bueno et al., 2024), thermal treatment (Mora, et al., 2019), chemical bath deposition (Flores-Carrasco et al., 2021), and many others, the main need is the development of a simple process which allows controlling the characteristics of the particles including the control of size, morphology and chemical composition, in a reproducible way, being of low industrial cost, continuous operation and high performance. Taking the above into account, the method that has managed to achieve these expectations to manufacture functional semiconductors with specific properties, suitable for new applications, has been the Polyol method (Martínez-Martínez et al., 2021; Flores-Carrasco et al., 2021).

Due to the approaches already presented, in this work were report the instrumentation of a system for the ZnO semiconductors manufacture by a Polyol-Mediated Thermolysis Process. Likewise, a systematic study of the experimental parameters has been carried out during the manufacturing process of the ZnO semiconductors, without forgetting the academic challenge of addressing manufacturing aimed at obtaining nanostructured semiconductor materials, due to the superior properties that these show, as well as contribute to a greater understanding of the influence of the configuration in the technique used on the morphological and structural characteristics of the ZnO semiconductors obtained.

METHODOLOGY

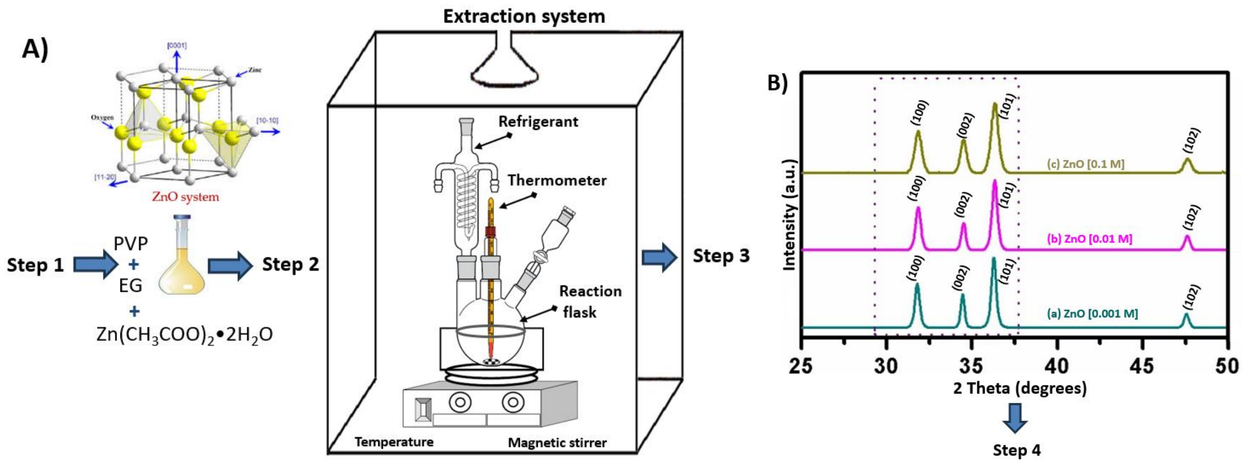
Manufacturing synthesis. As a first step, the stoichiometric amount of $Zn(CH_3COO)_2{\bullet}2H_2O$ and Polyvinylpyrrolidone (PVP) was dissolved in Ethylene Glycol (EG) in a three-necked flask fitted with a reflux condenser. Figure 1A shows the block diagram of the complete system of the Polyol-Mediated Thermolysis Process, employing for the ZnO semiconductors manufacture. Subsequently, the reaction solution thus obtained was stirred vigorously and then heated to a temperature of 185 °C. The reaction continued for 2 hours, after which the system was cooled to room temperature. The particles thus obtained were separated from the liquid by centrifugation and then washed repeatedly with deionized water. Finally, the particles were dried into a furnace out at 500 °C in an air atmosphere for 2 hours, and then a white powder sample of the zinc oxide precursor was collected.

Characterization techniques. X-Ray Diffraction (XRD) analysis was used to investigate the crystalline phase and structure of all the as-synthesized samples. These measurements have been performed on an X-Ray Diffractometer (Philips X´pert) with CuKα radiation (λ = 1.5406 Å) and over ther ange 2θ = 25-50° at room temperature. To study the morphology of all the as-synthesized samples, Scanning Electron Microscopy (SEM, FEI Teneo / EDAX-Dx4) analyses has been carried out employing an accelerating voltage of 5 kV.

RESULTS AND DISCUSSION

Figure 1B shows the XRD patterns of all the ZnO semiconductors manufacture, from the different concentration in the (0.001 M, 0.01 M, and 0.1 M) precursor solution. These patterns present the typical diffraction peaks that were assigned to the (1 0 0), (0 0 2), (1 0 1), and (1 0 2) planes of the ZnO structure (JCPDS data card no. 80-0075). Furthermore, the typical hexagonal (wurtzite) structure of all the ZnO semiconductors manufacture samples has been inferred from the XRD pattern, which is in good agreement with the intrinsic fundamental structure of ZnO as reported in the literature (Ramos-Justicia, et al., 2023; Flores-Carrasco et al., 2021, Bueno et al., 2024). No other crystalline phase was detected. Additional, it has been found that the intensity of the all peaks improvement with the increase in the concentration of the precursor solution, indicating that the crystalline quality also improved. Has been observed, also, that the Full Width Half-Maximum (FWHM) of the peaks became wider when increase the concentration of the precursor solution, indicating that the decreases particles sizes.

From the SEM micrographs shown in Figure 1C, has been study the morphology of all the ZnO semiconductor samples, independently of the initial reagent concentration used in each experiment. In Figure 1C(a), can be only observed in the SEM micrographs quasi-spherical particles agglomerated when the precursor a lower concentration has been used. In the case of 0.01 M concentration (Figure 1(b)), the SEM micrographs clearly revealed quasi-spherical, non-glomerated particles with a good size distribution, composed for subunits of nanometer-sized particles. When has been employing concentration of 0.1 M (Figure 1C(c)), it is possible to distinguish only the formation of monodisperse and dense particles with a nanometer-sized.



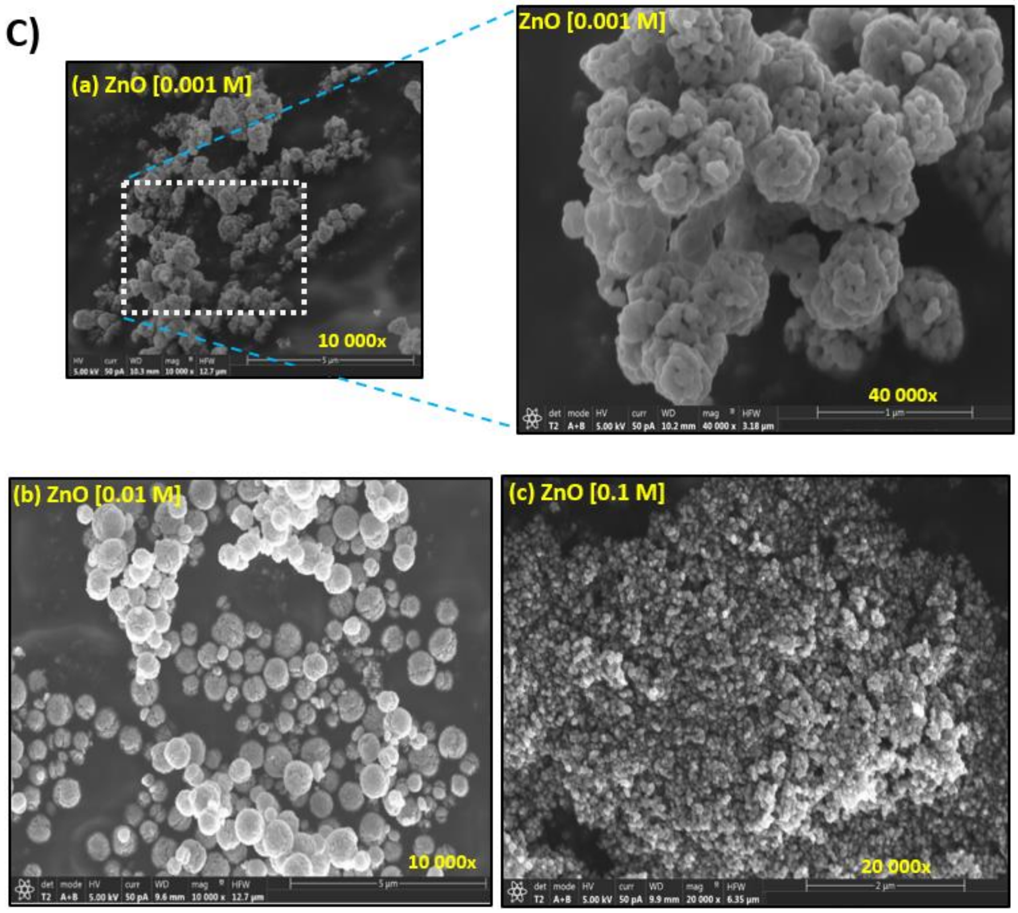


Figure 1: A) Schematic illustration of preparing for ZnO semiconductors. B) X-ray diffractograms of ZnO semiconductors manufactured in different concentration of precursor solution. C) SEM images of typical ZnO semiconductors.

CONCLUSIONS

XRD has been confirmed that all the manufactured semiconductors present the intrinsic fundamental structure of ZnO. The SEM images revealed that using the highest precursor concentration, the aggregation process does not occur and it is possible to obtain particles in the nanometric range.

Finally, the instrumented system by a Polyol-Mediated Thermolysis Process has been shown to successfully produce ZnO semiconductors in an efficient and reproducible form. What is evident from these findings is that the morphology and the particle size has been controlled, to help promote the large-scale production of these nanomaterials given their properties to allow various applications in subsequent studies.

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