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Article

Comparison of methods for obtaining a hydroxyapatite and zinc oxide composite (HAp/ZnO)

Comparación de métodos para la obtención de un compósito de hidroxiapatita y óxido de zinc (HAp/ZnO)

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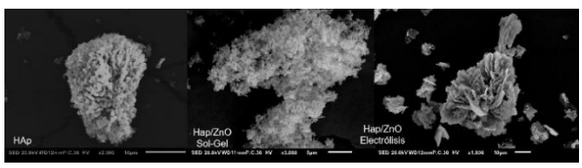
Abstract

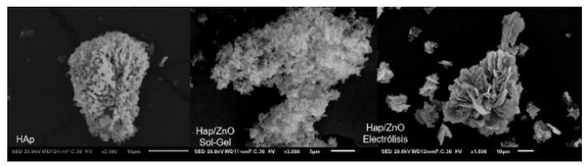
In this work, the synthesis of a composite material based on hydroxyapatite (HAp) and zinc oxide (ZnO) is reported. Two types of synthesis were evaluated, in order to know which of them allows to obtain a homogeneous composite material of HAp and ZnO, since making a composite material implies that two or more compounds must be integrated and do not separated; the HAp will be obtained from eggshell residue, ZnO will be synthesized by Sol-Gel and electrolysis; in the ZnO obtention, the previously synthesized HAp was incorporated and it is followed by a thermal treatment obtain the oxide. To evaluated the incorporation of ZnO with hydroxyapatite, Scanning Electron Microscopy, Elemental Analysis and Mapping by Energy Dispersive Spectrometry, Infrared Spectroscopy Analysis and X-ray Diffraction were performed. These two synthesis methods are aiming to obtain a homogeneous material, establishing a methodology to produce the material composite, as well as improve the photocatalytic properties.



Fintech, Transformation, Finance

Resumen

Este trabajo aborda la síntesis de un material compuesto con hidroxiapatita (HAp) y óxido de zinc (ZnO), se evaluarán dos tipos de síntesis para conocer cuál de ellas permite obtener un compósito homogéneo de HAp y ZnO, ya que el hacer un compósito implica que dos compuestos se integren sin separarse; la HAp se obtendrá del cascarón de huevo (residuo), el ZnO se obtendrá por síntesis Sol-Gel y electrólisis. Al realizar la síntesis del ZnO se incorporó la HAp previamente sintetizada y se dio el tratamiento térmico para obtener el óxido. Para evaluar la incorporación de ZnO en la HAp se realizó Microscopía Electrónica de Barrido, Análisis Elemental y Mapeo por espectrometría de Energía Dispersiva, Análisis de Espectroscopia de Infrarrojo y Difracción de rayos X. Al realizar estos métodos de síntesis se busca obtener un material homogéneo, establecer una metodología para obtener el compósito y mejorar las propiedades fotocatalíticas.



Fintech, Transformación, Finanzas

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Introduction

Currently, it is important to search different chemical routes for material synthesis, this approach allows for the development of synthetic materials using methodologies that reduce or eliminate wastes, employing environmentally friendly processes. These materials can be used in various fields, such as photocatalysis, antibacterial materials, biomedical applications, among others (Marinas A., 2007), (Doria S., 2009), (Hernández L. , M., & Prierto S., G., 2017).

Zinc oxide (ZnO) is a semiconductor with an exciton binding energy of 60 meV and a band gap energy of 3.37 eV, emitting exclusively in the UV range and exhibiting piezoelectricity. This oxide is biocompatible, making it suitable for biomedical, antibacterial, UV protection, optoelectronic, and catalysis applications (Wen, T., Gao, J., Shen, J., y Zhou, Z., 2001).

Hydroxyapatite (HAp) is basically composed of calcium and phosphorus, although depending on the synthesis method, it may contain traces of elements such as sodium and magnesium. One of the main characteristics of this material is the calcium-phosphorus molar ratio; the lower the ratio, the higher the acidity and solubility of the samples, which is also a factor related to the mechanical properties of the material. Pure-phase HAp has a Ca/P molar ratio of 1.67 and exhibits greater stiffness compared to HAp with a different molar ratio. When the ratio is 1.5, calcium-deficient samples are obtained, and if the molar ratio is higher than 1.67, it contains carbonate groups and traces of Mg. Additionally, HAp with molar ratios ranging from 1.5 to 2.0 has been used as ceramic coatings (Enríquez P. M. A., Castrejón S. V. H, Rosales D. J., Díaz C. F. J. A., 2020), (H. Dai, T. Xinwei , H. Zhu, T. Sun y X. Wang , 2018).

It is important to highlight that in the quest to improve various materials, oxide composites with supports or coupled materials have emerged, such as reinforced rubber, mortar and concrete, alloys, porous and fractured media, fiber composites, polycrystalline aggregates (metals), heterogeneous catalysts, and so on (Campbell, 2010), (Hashin, 1983).

Zinc oxide and hydroxyapatite have been integrated into composite materials (Sowińska-Baranowska, A., & Maciejewska, M., 2024) (Gupta, R., Singh, V. P., & Agarwal, M., 2024). In 2015, Ochoa-Fajardo D.A. synthesized a zinc oxide composite impregnated in a granular support that exhibited photocatalytic activity. The photocatalytic of ZnO was taken in advantage by using two granular supports (activated carbon and andesite) and two impregnation methods (controlled precipitation and solvent evaporation) (activated carbon and andesite) and two impregnation methods (controlled precipitation and solvent evaporation) (Fajardo, 2015). In 2016, Gálvez-Co et al. developed hydroxyapatite doped with ZnO nanoparticles for potential biomedical applications. Gálvez-Coy obtained natural hydroxyapatite from bone and studied the antimicrobial activity of the samples against Pseudomonas aeruginosa ATCC 9027 and Staphylococcus aureus ATCC 25923 (Gálvez-Coy, 2016). In 2019, Charlena *et al.* realized the synthesis and characterization of Zinc Oxide/Hydroxyapatite to obtain an antibacterial biomaterial. The hydroxyapatite was made from Snail shells (Bellamya javanica) due to their high calcium content, and the ZnO was synthetized using the low-temperature hydrothermal method (Charlena, Suparto, & Kurnia, 2019).

For photocatalysis, the formation of composites has been implemented, as modifying the properties of the main compound with another material can meet specific requirements. There are many methods available for the preparation of zinc oxide composites, which are divided into hydrochemical and pyrotechnical methods (Fajardo, 2015), (Iglesias-Juez, A., Kubacka, A., Colón, G., y Fernández-García, M., 2013), (Rashtiani, M., Ghasemi, E., Hallajian, S., & Ziyadi, H., 2024) (Das, A., Ringu, T., Ghosh, S., & Pramanik, N., 2024) (El Bekkali, C., Abbadi, M., Labrag, J., Es-saidi, I., Robert, D., Nunzi, J. M., & Laghzizil, A., 2024).

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Among the hydrochemical and pyrotechnical methods for composite synthesis, notable techniques include solution impregnation (Zhong, J. B., Li, J. Z., He, X. Y., Zeng, J., Lu, Y., He, J. J., y Zhong, F., 2014), controlled precipitation (Ngo, G. V., Margaillan, A., Villain, S., Leroux, C., y Bressy, C. , 2013), microwave-assisted synthesis (Assi, N., Mohammadi, A., Sadr Manuchehri, Q., y Walker, R. B., 2014), hydrothermal deposition (Sahoo, T., Kim, M., Baek, J. H., Jeon, S .- R., Kim, J. S., Yu, Y .- T., ... Lee, I .-H., 2011), composite synthesis in emulsion (Lim, B. P., Wang, J., Ng, S. C., Chew, C. H., y Gan, L. M., 1998), mechanical mixing (Mohammadi, M., Sabbaghi, S., Sadeghi, H., Zerafat, M. M., y Pooladi, R., 2014), solvent evaporation (Shahid, M., McDonagh, A., Kim, J. H., y Shon, H. K., 2014), and physical vapor deposition (Thangadurai, P., Zergioti, I., Saranu, S., Chandrinou, C., Yang, Z., Tsoukalas, D., Boukos, N., 2011). . In this work, hydroxyapatite was synthesized, zinc oxide was produced using sol-gel synthesis (Contreras-de La Cruz, M. A., García-González, N., Enríquez-Pérez, Ma. Ángeles And Castrejón-Sánchez, V. H., 2022) and electrolysis synthesis with zinc electrodes (Castrejón-Sánchez, V. H., Gacía-González, N., Enríquez-Pérez, Ma. Ángeles and Hernández-Bernardino, B., 2021), and hydroxyapatite was incorporated into the precursors of each zinc oxide synthesis.

Methodology

Materials

Eggshell, Hydrogen Peroxide (90%, Sigma Aldrich), Phosphoric Acid (85%, Sigma Aldrich), distilled water, zinc acetate, oxalic acid, sodium chloride.

Synthesis was carried out in two stages: in first stage, the materials were obtained separately. For second stage, the composite was prepared using sol-gel and electrolysis together. The methodology used is described below.

HAp Synthesis

For HAp synthesis, eggshells were collected, washed, and dried. They were treated with a 30% H_2O_2 solution at 95°C for 1 h, followed by washing the material with distilled water.

The material was dried at 80°C for 48 h. Subsequently, it was impregnated with 1M H_3PO_4 using the methodology proposed by Enríquez (Enríquez P. M. A., Castrejón S. V. H, Rosales D. J., Díaz C. F. J. A., 2020). The material was calcined at 800°C for 2 h.

ZnO Synthesis

Sol-Gel synthesis

Two solutions were prepared: Solution A: zinc acetate was dissolved in ethanol and heated to 60°C for 1 h. Solution B: oxalic acid was mixed in ethanol and heated to 50°C for 1 h; both solutions were stirred constantly. Solution A was added to Solution B, forming a gel, which was dried at 80°C for 20 h. Finally, the material underwent a thermal treatment at 650°C for 30 min, resulting in ZnO powders, which were labeled for characterization.

Electrolysis Synthesis

Sodium chloride was dissolved in water, and this solution was placed in an electrochemical cell, with zinc as both the anode and cathode. The solution was stirred for 30 min at 19 V and 0.33 Amp. The sample was then washed and filtered, followed by thermal treatment at 450°C for 2 h. The resulting ZnO was labeled for characterization.

Composite Synthesis

The composite was obtained by preparing HAp as described previously and it is pour into the electrochemical cell used for ZnO synthesis and the electrochemical process is repeated. The resulting material was then washed and filtered, followed by heat treatment for 2 h at 450°C, yielding a powder of the HAp/ZnO composite, which was labeled for characterization.

Sol-Gel Methodology

Zinc acetate was mixed with ethanol, and the solution was stirred and heated to 60°C for 45 min. HAp was then added, and the mixture was stirred for 15 min. Separately, a solution of oxalic acid with ethanol was prepared and stirred for one h at 50°C. Afterward, the two solutions were combined, forming a gel that was dried at 80°C for 20 h.

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Finally, the obtained material was calcined at 650°C for 1 h, resulting in a powder. The HAp/ZnO composite was labeled for characterization.

Electrolysis Synthesis

Sodium chloride and HAp were dissolved in water, and the solution was stirred for 30 min. The solution was placed in an electrochemical cell, where both the anode and cathode were zinc. The electrolysis process was carried out for 30 min, with the sample under constant stirring at 19 V and 0.33 amperes.

Material characterization

The characterization of HAp, ZnO, and the composites was carried out using the following techniques: X-Ray Diffraction (XRD) to determine the crystallographic planes of the material, using a Bruker DXR Discover D8 model, obtaining a diffractogram in the range from 15° to 90° range in 2θ geometry. Fourier-Transform Infrared Spectroscopy (FTIR) was used to identify the functional groups present; a Perkin Elmer UART Two spectrophotometer was used, with spectra ranging from 4000 to 500 cm^{-1}. Scanning Electron Microscopy (SEM) was employed to analyze the morphology of the materials and their elemental composition via Energy Dispersive Spectroscopy (EDS), using a JEOL JSM-IT100 Scanning Electron Microscope coupled with a Bruker Nano D-12489 probe, operating at 20 kV acceleration voltage, high vacuum, and secondary electron signal.

Results and Discussion

In Figures 1 to 3, the micrographs of the individual components that compose the HAp/ZnO composite can be observed. The goal is to understand the effect that the synthesis process has on the morphology of each component and whether these morphologies are retained when the composite is obtained.

Figure 1 is a micrograph corresponding to HAp, which is the result of the chemical treatment with phosphoric acid and the subsequent heat treatment of calcium carbonate derived from eggshell.

The morphology of the HAp (which will serve as the composite's support) closely resembles coral, which has been previously reported (N. Mohan, R. P. F. B. Fernandez y H. Varm, 2018), (Contreras-de La Cruz, M. A., García-González, N., Enríquez-Pérez, Ma. Ángeles And Castrejón-Sánchez, V. H., 2022). According to Mohan et al. (N. Mohan, R. P. F. B. Fernandez y H. Varm, 2018), these types of porous morphologies are the result of the controlled evolution of CO_2 gas during the reaction between calcium carbonate and the phosphate group in the phosphoric acid solution.

Box 1

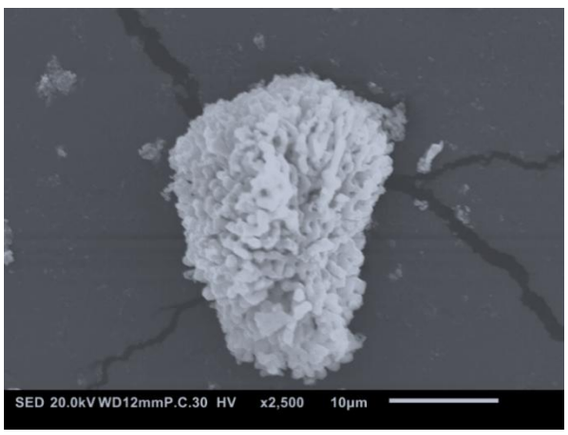

Figure 1
Hydroxyapatite Micrograph
Source: own elaboration

The sol-gel process allowed to produce a particulate material that does not exhibit a predominant morphology (Figure 2).

The ZnO particles show relatively flat and continuous surfaces, which may present a clear disadvantage in the photocatalysis process in which they will be used. The particle sizes obtained through this method range from 15 to approximately 175 µm.

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Box 2

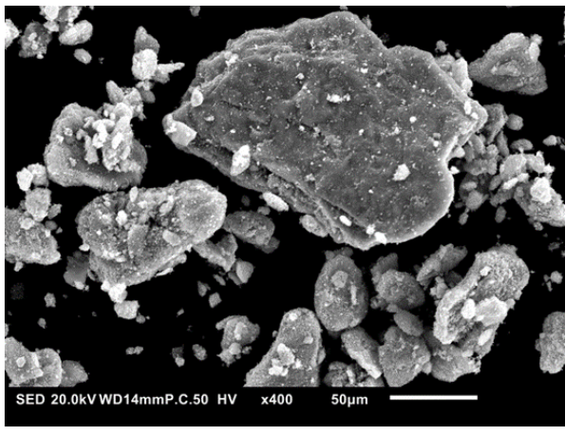

Figure 2
ZnO Sol-Gel Micrograph
Source: own elaboration

The ZnO obtained by electrolysis (Figure 3) exhibits a highly irregular surface and appears to be quite porous. This characteristic could be an advantage for ZnO, as in the photocatalytic processes where it will be used, porosity is accompanied by a larger surface area compared to a material with a continuous surface. The size of the ZnO particles ranges from 40 to 70 µm.

Box 3

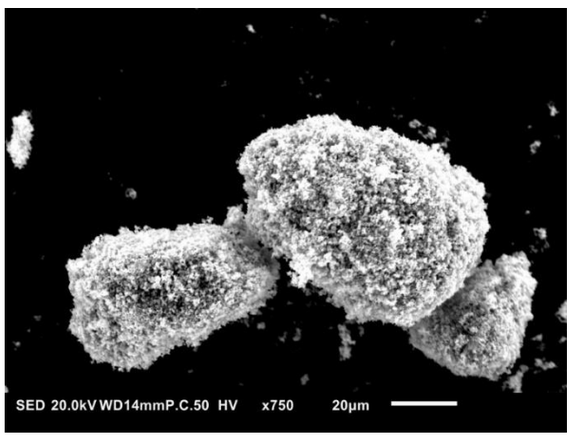

Figure 3
ZnO Electrolysis Micrograph
Source: own elaboration

Elemental Analysis

Energy Dispersive Spectroscopy (EDS) was performed to analyzed the elemental composition of the composites and individual compounds. When comparing the atomic percentages of the individual components, the ZnO synthesized by electrolysis is very similar to that obtained by sol-gel synthesis, with stoichiometries close to the 1:1 atomic ratio.

The atomic Ca/P ratio for HAp is 38.11, in the Sol-Gel composites it was 8.91, and 66.25 for Electrolysis,respectively; this ratio increases with the rise in carbonate ion content, as the CO_3^{2-} ion replaces PO_4^{3-} (Ochoa I.,López E., Copete H., 2021), these ratios indicate that the hydroxyapatite is both hydroxylated and carbonated (Markovic, M., Fowler, B. O., & Tung, M. S., 2004).

Additionally, the Ca/Zn ratio in the composites was calculated, with a value of 2.38 for Sol-Gel, indicating that there are approximately two Ca atoms for each Zn atom. For Electrolysis, the ratio is 33.13, meaning there are approximately 33 Ca atoms for each Zn atom. These ratios are associated with the formation of composites (Contreras-de La Cruz, M. A., García-González, N., Enríquez-Pérez, Ma. Ángeles And Castrejón-Sánchez, V. H., 2022).

In the composites, it is observed that zinc decreases according to the type of synthesis having 3.04% At. for HAp/ZnO Sol-Gel and 0.4% At. for ZnO/HAp Electrolysis. We assume that it is because the sol-gel technique allows better incorporation between ZnO and HAp.

Sol-Gel Composite

Figure 4 corresponds to the HAp composite with ZnO obtained by sol-gel. The displayed morphology for this material appears without a defined structure, differing significantly from the morphologies of the individual HAp and ZnO components (Figures 1 and 2, respectively). A surface mapping of the particle was conducted to determine the distribution of ZnO on the HAp support (Figure 5), where the green color is associated with Zn from ZnO and the orange with Ca from $CaCO_3$.

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Box 4

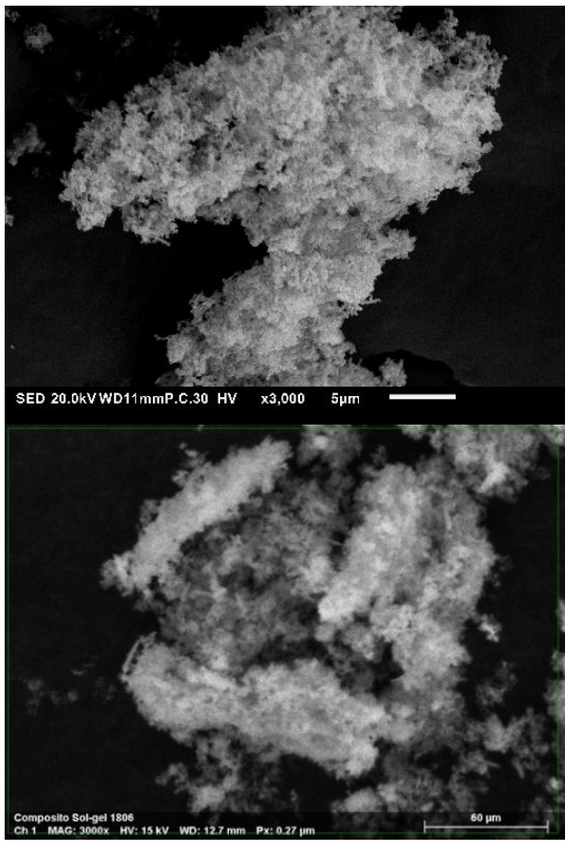

Figure 4
HAp/ZnO Sol-Gel Micrograph
Source: own elaboration

It is evident that the distribution of ZnO on the surface of $CaCO_3$ is quite homogeneous, as shown in Figure 5. The micrograph's background was removed to make the distribution of the elements clearer.

Box 5

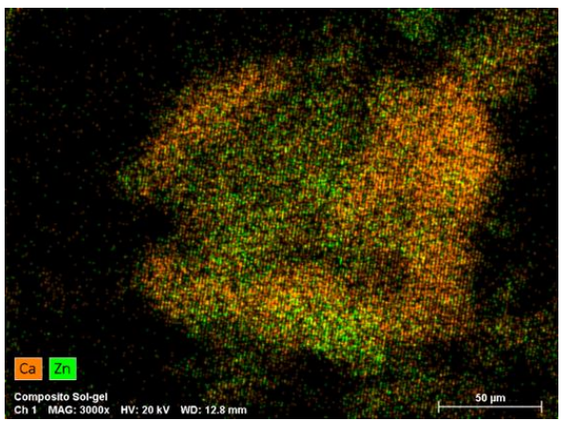

Figure 5
HAp/ZnO Sol-Gel Mapping
Source: own elaboration

Electrosynthesis Composite

For the composite obtained through electrosynthesis, elemental mapping was also performed, like the previous composite. In the micrograph in Figure 6, the morphology of the HAp/ZnO composite can be observed. In this case, the morphology resembles flakes, which is very different from the morphology of both HAp and ZnO.

Box 6

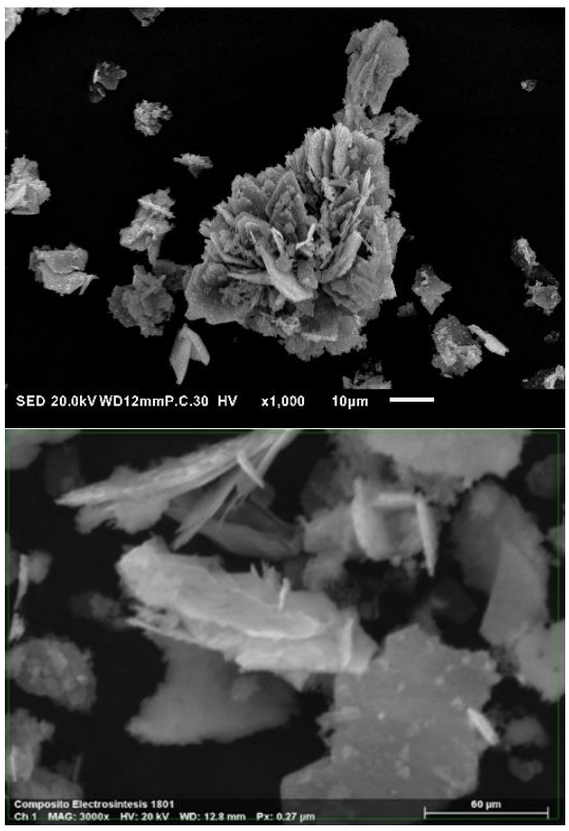

Figure 6
HAp/ZnO Electrolysis Micrograph
Source: own elaboration

Figure 7 represents the distribution of ZnO (green) on the HAp support indicated in orange, which shows that the distribution of ZnO on the surface of HAp is less homogeneous than in the previous case, as there are many areas of HAp (orange) without ZnO on its surface. To improve the visualization of the compounds' distribution, the background micrograph in Figure 7 was removed.

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Box 8

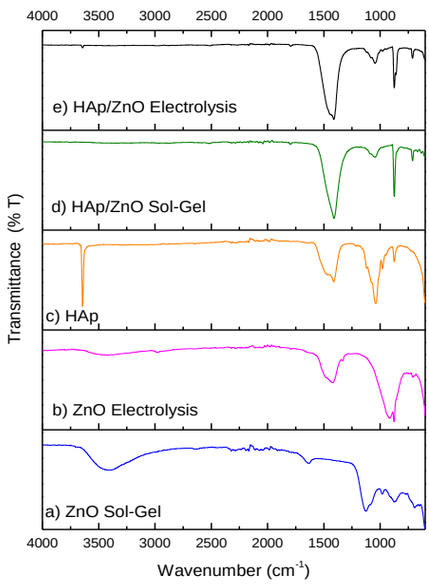

Figure 8
Spectra of FTIR

Source: own elaboration

Box 7

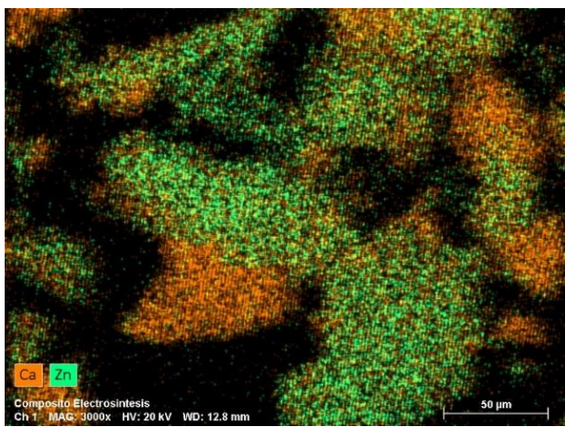

Figure 7
HAp/ZnO Electrolysis Mapping

Source: own elaboration

FTIR Spectroscopy

Figure 8 shows the FTIR spectra of the samples. Both techniques confirm the formation of ZnO, with small shifts in the absorptions.

When ZnO is prepared by sol-gel, the peaks at 3404 cm^{-1} and 1651 cm^{-1} correspond to OH stretching vibrations and bending modes of absorbed water (Sowri, Ramachandra, Sujatha, Venugopal, & Mallika, 2013).

The vibrations at 1131 cm^{-1}, 966 cm^{-1}, 883 cm^{-1}, and 646 cm^{-1} are due to the tension of the Zn-O bond, indicating the formation of ZnO (Awasthi, Adhikari, Ko, Park, & Kim, 2016) (Galindo G., Fortis H., De La Rosa R., Zermeño G., & Galindo G., 2022), (Maher, S.; Nisar, S.; Muhammad A., S.; Saleem, F.; Behlil, F.; Imran, M.; Assiri, M. A.; Nouroz , A.; Naheed, N.; Khan, Z. A. ; Aslam, P., 2023).

By electrolysis (Figure 8b), the signal at 3456 cm^{-1}, which corresponds to the OH bending stretch of absorbed water (Sowri, Ramachandra, Sujatha, Venugopal, & Mallika, 2013), is predominant. The Zn-O bond tension is observed at 914 cm^{-1}, 873 cm^{-1}, and 705 cm^{-1}, characteristic signals of ZnO formation (Faria, y otros, 2022). We assume that these shifts are due to the fact that the precursors used in this synthesis cannot be completely eliminated.

In Figure 8c, the peak at 3632 cm^{-1} corresponds to the stretching of the hydroxyl group associated with the OH group of HAp. The absorption at 1412 cm^{-1} is due to the presence of carbonate groups, and at 1040 cm^{-1}, characteristic of phosphate groups. The signal at 880 cm^{-1} is attributed to the presence of both carbonate and phosphate groups, characteristic signals of HAp (Adeogun, y otros, 2018).

The ZnO/HAp composite, regardless of the preparation technique, essentially shows the same signals with slight shifts (see Figures 8d and 8e). The presence of ZnO influences the vibrations of HAp due to steric hindrances, leading to a reduction in the vibrational energy of the HAp molecule (Molodovan M, 2015).

The intensity of the 3632 cm^{-1} band decreases because of the interaction between ZnO and the OH groups of HAp (Charlena, Suparto, & Kurnia, 2019); the absorption of carbonate groups at 1420 and 833 cm^{-1} is more intense due to the interaction between the materials (Azam A, 2012), (Molodovan M, 2015). The absorption at 1019 cm^{-1}, attributed to phosphate groups, decreases because of the interaction between ZnO and PO_4, indicating that HAp is influenced by Zn (Molodovan M, 2015) (Charlena, Suparto, & Kurnia, 2019) . The absorption bands of ZnO present in the material before mixing with HAp do not appear in the FTIR spectrum, except for a band at 646 cm^{-1} at lower wavenumbers.

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The prepared composites exhibit homogeneity, this means that ZnO and HAp are well combined (Charlena, Suparto, & Kurnia, 2019) (Azam A, 2012).

X-ray diffraction

Figure 9 shows the results for X-Ray Diffraction analysis of the composites (HAp/ZnO Sol-Gel and ZnO/HAp Electrolysis) and the precursors HAp, ZnO Sol-Gel, and ZnO Electrolysis.

The ZnO (Figure 9a and 9b) displays 2θ peaks at 31.9°, 34.6°, 36.4°, 47.8°, 56.8°, 68.3°, and 69.4°, with their respective diffraction planes (-100), (00-2), (-10-1), (-10-2), (-210), (-21-2), and (-20-1), respectively. These angles are characteristic of the hexagonal Wurtzite phase of ZnO previously reported (Alami, Z., Salem, M., Gaidi, M., & Elkham, J., 2015), (Baneto, M., Enesca, A., Lare, Y., Jondo, K., Napo, K., & Duta, A., 2014), (Carta de difracción COD-2300113, Sowa Heidrun, Ahsbahs Hans, 2006).

Figure 9c shows the diffractogram of HAp, with the peaks at 2θ angles of 19.6°, 28.99°, 46.66°, 51.1°, 54.7°, and 63°, along with their respective reported diffraction planes (El hadad, A. A.; Barranco, V.; Jiménez M., A. ; Peon, E.; Galván, J. C., 2010), (Hendricks S., Jefferson M., Mosley V., 1932), (Carta de Difración COD 1100066: Al_2O_3-ZrO_2 standar).

Since it is a carbonated HAp, it is possible that Zn ions occupy the sites corresponding to the CO_3^{2-} y PO_4^{3-}ions. When HAp and ZnO are coupled, the signals become broader, and the intensity increases (see Figure 9d and 9e). Contreras-de La Cruz, M. *et Al.* (Contreras-de La Cruz, M. A., García-González, N., Enríquez-Pérez, Ma. Ángeles And Castrejón-Sánchez, V. H., 2022) also confirmed that both signals shift slightly, which is also observed in the infrared spectrum (Figure 8d and 8e).

Box 9

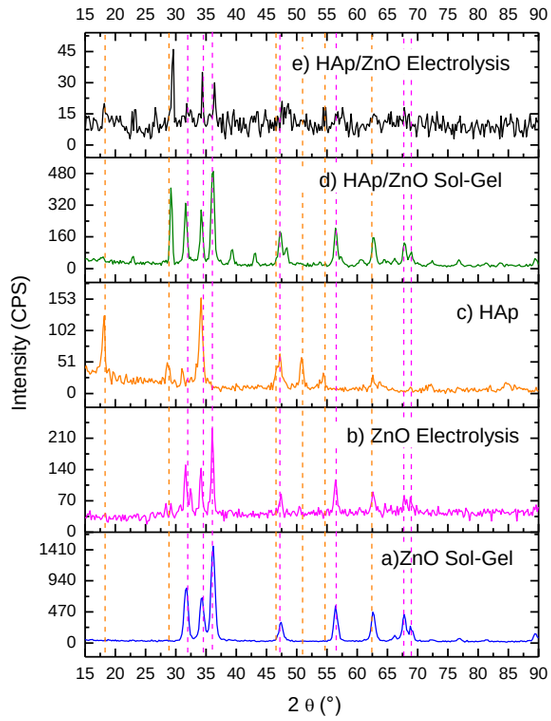

Figure 9
Diffractograms
Source: own elaboration

Conclusions

The HAp/ZnO composite was obtained through two synthesis routes (Sol-Gel and Electrolysis); to achieve homogeneity, hydroxyapatite was added during the preparation of the ZnO precursor, followed by a thermal treatment.

In the scanning electron microscopy images, the influence of the synthesis method on morphology is evident. Through electrolysis, the formation of agglomerated sheets is observed, whereas in the Sol-Gel method, no defined morphology is seen, and only pores are observed, which could facilitate the photocatalytic process. The elemental analysis allowed the quantification of the atomic percentages of each composite, showing that the Zinc drastically decreases in the Electrolysis composite (0.4% At) in comparison with the Sol-Gel composite with a Zn content of 3.04% At. The mapping shows that Zn and Ca are homogeneously distributed, where Zn associated with ZnO and Ca with HAp.

Infrared spectroscopy confirmed the formation of both composites; however, it is not possible to distinguish between them.

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The X-ray diffraction analysis confirmed the presence of HAp and ZnO in both composites. The crystallinity of the Electrolysis composite decreased, which may be associated with the morphological changes and the reduction in the atomic percentage of Zn.

Declarations

Conflict of interest

The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence the article reported in this article.

Author contribution

Dávalos-Rosas, V. G.: Contributed to the synthesis of the materials studied in the article.

García-González, N.: Contributed to the project idea, the characterization, and the discussion of the results of the materials studied in the article.

Enríquez-Pérez, Ma. Angeles: Contributed to the project idea, the characterization, and the discussion of the results of the materials studied in the article.

Castrejón-Sánchez, V.H.: Contributed to the project idea, the characterization, and the discussion of the results of the materials studied in the article.

Availability of data and materials

The synthesized materials and all the data from the analyses carried out in this research are available.

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Abbreviations

DXR	X-ray diffraction
EDS	Energy Dispersive Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
HAp/ZnO Electrolysis	Composite synthesized by Electrolysis.
HAp/ZnO Sol-Gel	Composite synthesized by Sol-Gel.
HAp	Hydroxyapatite
SEM	Scanning Electron Microscopy.
ZnO	Zinc Oxide

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