

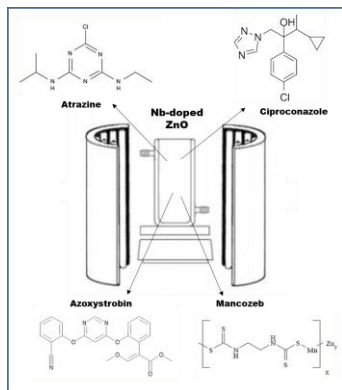
Enhancing the Photocatalytic Potential of Zinc Oxide in Pesticides Degradation through Niobium Doping

ORAL/POSTER

Ph.D. Student: Y/N

Journal: NONE

C. Erhardt¹, A. Alves¹, T. Oliveira². (1) Federal University of Rio Grande do Sul Porto Alegre, Brazil, camilaerhardt1@gmail.com (2) Federal University of Health Sciences of Porto Alegre, Porto Alegre, Brazil



With their high surface area and chemical reactivity, photocatalysts play a crucial role in removing pesticides from contaminated water and soil. Nanostructured zinc oxide doped with niobium, manufactured through ultra-rapid microwave-assisted hydrothermal synthesis, has shown promise in this context. Doping with varying concentrations of niobium pentachloride resulted in crystalline and morphological structure modifications, as evidenced by X-ray diffraction (XRD), SEM and Raman analysis. The band gap in the 3.21 to 3.29 eV range indicates suitable potential for photodegradation applications. Niobium doping had a positive impact, as evidenced by the observed improvement in superficial areas with increasing dopant concentration. Photocatalysis assays were conducted with four different pesticides, confirming the photocatalytic potential of the material and allowing for analysis of the resulting reaction products, thereby highlighting the effectiveness of the doped photocatalyst for pesticide removal.

Introduction

The increasing use of pesticides in agriculture has raised environmental concerns due to agricultural effluents' contamination of soils and water resources. These chemical compounds, such as Atrazine, Mancozeb, Azoxystrobin, and Ciproconazole, are persistent and highly toxic despite being effective in pest control. In this context, advanced oxidative processes (AOPs) emerge as a promising alternative for removing organic pollutants[1]. Among AOPs, heterogeneous photocatalysis using semiconductors like zinc oxide (ZnO) is particularly notable. ZnO, with its wurtzite crystal structure and wide bandgap, is an effective material for photocatalytic reactions when exposed to ultraviolet (UV) light [2]. Doping ZnO with niobium (Nb) has been explored to enhance its catalytic properties. Niobium can modify the crystal structure of ZnO, increasing its photocatalytic activity and chemical stability [3]. Additionally, the presence of niobium ions in the ZnO structure can facilitate the capture of electrons and holes generated during UV light excitation, reducing charge recombination and enhancing the efficiency of pesticide photodegradation.

Material and Methods

Zinc nitrate (Synth, 98%), ammonium hydroxide (Dynamics, P.A.), and ultrapure Type 1 water ($\sigma = 0.054 \mu\text{S cm}^{-1}$ at 25 °C) were utilized in the experiment. Niobium pentachloride, in varying concentrations (1%, 3%, and 6%) relative to the mass of zinc nitrate, was added to a 0.2 M aqueous zinc nitrate solution. Ammonium hydroxide was then incrementally added to adjust the pH to 8. The solution was thoroughly mixed under magnetic stirring for 10 minutes and subjected to treatment in a SINEO microwave model MDS-8G at 200 °C for 5 minutes. The resulting precipitate was centrifugated and washed repeatedly with ultrapure water. Subsequently, the powders were dried in an oven at 110 °C. In the

photodegradation assays, the solution containing the pesticide and the photocatalyst was exposed to light emitted by 12 blacklight lamps, each rated at 8 W (Fluor BLB T5, Sadokin), totaling 96 W. For this purpose, the catalyst (0.01 - 1 g) was added to 100 ml of the pesticide's aqueous solution, with concentrations ranging from 2 to 20 ppm. Four pesticides, Atrazine, Mancozeb, Azoxystrobin, and Ciproconazole, were analyzed. The degradation occurred under air bubbling, and approximately 5 mL aliquots of the mixture were collected and filtered through a polysulfone membrane with 0.22 μm pores to monitor the decrease in solution concentration over time. Liquid chromatography analyses were then performed to assess the difference in concentration between the initial and final stages and to analyze the products generated during photodegradation.

Results and Discussion

Several analyses were conducted to confirm the formation of ZnO nanoparticles and their doping with Nb via microwave-assisted hydrothermal synthesis. X-ray diffraction (XRD) was utilized to examine the crystalline phases of ZnO. Figure 1 illustrates the diffractograms of pure ZnO powders and those with various dopant concentrations. The primary phase observed in the XRD patterns corresponds to the hexagonal wurtzite structure of ZnO (ICSD No. 010897102). The characteristic peaks associated with the wurtzite-like structure, identified by Miller indices, are located at 31.8° (100), 34.5° (002), 36.3° (101), 47.6° (102), and others. All samples primarily consist of zinc oxide, consistent with previous studies. Scanning Electron Microscopy (SEM) was employed to assess the morphologies of the samples. Figure 2 displays micrographs illustrating both undoped and Nb-doped ZnO. The presence of rod-like morphologies is clearly evident and corroborated by existing literature [4].

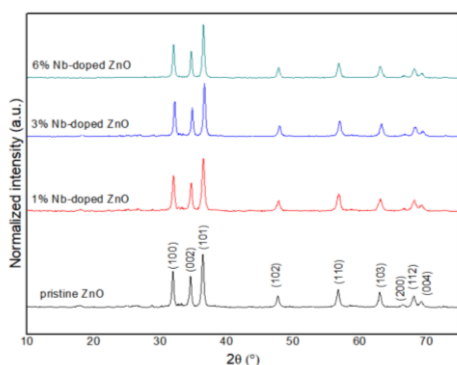


Figure 1. X-ray diffractograms of undoped and Nb-doped ZnO

According to the results obtained from Raman spectroscopy, there is a shift in the main vibrational mode found at 427 cm^{-1} from the pure zinc oxide sample to the niobium-doped zinc oxide. This shift indicates a crystal lattice distortion, likely due to doping. Additionally, there is an additional vibrational mode in the samples doped with niobium, suggesting the presence of a second phase corresponding to niobium oxide excess within the structure.

Regarding the surface area, there is a tendency for an increase in dopant concentration to lead to an increase in surface area. Pure zinc oxide obtained a surface area of $5,448\text{ m}^2/\text{g}$, while zinc oxide with 6% niobium reached $75,582\text{ m}^2/\text{g}$. The same trend is observed with the bandgap. As the niobium doping increases, the band gap widens, ranging from 3.21 to 3.29 eV.

Conclusions

The analyses confirmed the formation of ZnO nanoparticles and their doping with Nb through microwave-assisted hydrothermal synthesis. X-ray diffraction was employed to analyze the formation of crystalline phases of ZnO, revealing the predominance of the hexagonal wurtzite structure, which is consistent with previous studies. Scanning electron microscopy analysis allowed for evaluating sample morphologies, highlighting changes induced by niobium doping, as corroborated by Raman analysis. Increases in surface area and bandgap were observed with increasing dopant concentration, indicating a direct relationship between doping, structural properties, and the photodegradation of pesticides. These findings suggest that the synthesis of doped ZnO can be optimized for photocatalytic applications, with significant potential in environmental remediation.

Acknowledgments

The authors would like to thank the National Council for Scientific and Technological Development (CNPq) and the Coordination for the Improvement of Higher Education Personnel (CAPES) for their financial support.

References

- [1] Z.U.H. Khan, N.S. Gul, S. Sabahat, J. Sun, K. Tahir, N.S. Shah, N. Muhammad, A. Rahim, M. Imran, J. Iqbal, T.M. Khan, S. Khasim, U. Farooq, J. Wu, *Ecotoxicol Environ Saf* 267 (2023).
- [2] C. Stockey Erhardt, W. Guaglianoni, A.P. Garcia, T.M. Basegio, C.P. Bergmann, *Ceram Int* (2022).
- [3] J.M.P. Silva, R.S. Julião, T.C.N. Nicácio, M.C.N. Melo, R.M. Santos, M.R.D. Bomio, F. V. Motta, *J Alloys Compd* 985 (2024).
- [4] N. Pushpa, M.K. Kokila, *Mater Today Proc* (2024).

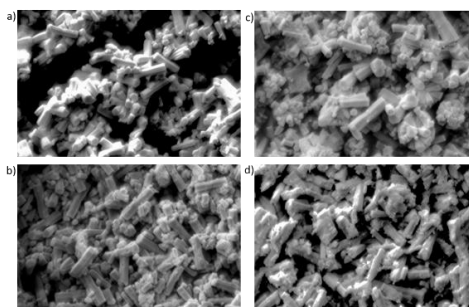


Figure 2. SEM images of the a) pristine ZnO powder, b) 1% Nb-doped ZnO, c) 3% Nb-doped ZnO and d) 6% Nb-doped ZnO

The experiments were carried out in triplicate using the four pesticides, wherein their degradation potential was assessed in the presence and absence of UV light. The results revealed a significant relationship between the dopant concentration and the rate of pesticide photodegradation. This increase in photodegradation potential is primarily attributed to the enhanced surface area of the nanostructured material.