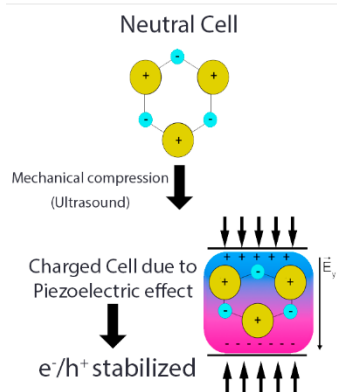


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Piezoelectric Bismuth Niobate samples were synthesized by the hydrothermal method, and thermally treated at 500 and 700 °C. α -BiNbO₄ and Bi₅Nb₃O₁₅ crystalline phases were indexed successfully to the samples treated at 500 °C and 700 °C respectively. The samples presented up to 50% increase in photodegradation rates of Methylene Blue and Methanol when assisted by ultrasound. The piezoelectric effect promotes a more efficient charge separation than single photoexcitation, showing promising results for applications in Piezo-Photocatalysis.

Introduction

As an advanced oxidation process, photocatalysis has gained prominence in energy and environmental remediation by presenting the possibility of direct solar energy utilization for dye and organic pollutant degradation. The so-called Piezocatalysis, a recently emerging field, takes advantage of the Piezoelectric effect, where non-centrosymmetric materials are able to generate electric fields from mechanical stimuli [1,2]. Piezo-photocatalysis combines the advantages of both, where photogenerated charges gain additional stabilization by the generated electric field, enhancing photocatalytic activity[1].

Despite its great potential, applications and prospects of piezo-photocatalysts remain largely unexplored. This work aims to evaluate the effect of piezoelectric properties in the photocatalytic activities of Bismuth Niobate samples.

Material and Methods

Bismuth Niobate Samples were prepared by an hydrothermal synthesis at pH 8, 200 °C and 150 psi for 24 hours, using 8 mL of a 2 M HNO₃ solution containing 5 mmol of Bi(NO₃)₃ (Aldrich) and 40 mL water solution containing 5 mmol of niobium ammonium oxalate (CBMM). After the hydrothermal process, the sample were thermally treated at 500 °C and 700 °C. The Photocatalytic and Piezo-Photocatalytic performances were evaluated by Methylene Blue and Methanol degradation assays under 100 mW.cm⁻² white light illumination. In order to perform the Piezoelectric assays an Ultrasonic horn was used, with a 15 seconds on/off cycle, and 50% intensity (65 W) in order to produce the mechanical stress.

Results and Discussion

XRD Analysis (Fig. 1) show the cristaline structure of

the prepared samples, where the heat treated samples show cristal structures in accordance with the α -BiNbO₄ phase (500 °C) and a mixture between α and Bi₅Nb₃O₁₅ phases (700 °C)[3,4].

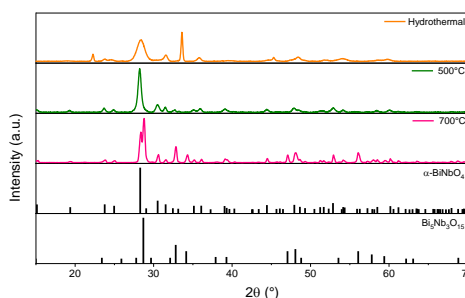


Figure 1. XRD data for the obtained samples.

Methylene blue and methanol photodegradation assays were conducted under the same irradiation conditions (100mW.cm⁻²). In both instances a 0,1 mg.ml⁻¹ catalyst suspension was used, where in methylene blue assays a 10⁻⁵ M solution of the dye was used. Additionally, the suspension was left in the dark for 60 min to ensure dye adsorption, being posteriorly irradiated for 3 hours (Fig. 3-5). For methanol assays a 10% MeOH/H₂O solution was used, and the suspension was irradiated for 4 hours (Fig. 6). For methanol assays, the formaldehyde formation was spectrophotometrically probed by using the Nash's reagent [5].

The piezo-photocatalytic assays reveal the synergic effect of employing the piezoelectric properties of the Bi(III) niobate. The results are more pronounced for

the sample heated at 700°C in which a mix between two crystalline phases are found. Preliminary EPR analysis of the system with DMPO spin-trapping show a high preference for direct oxidation of the substrate, where DMPOX* was preferentially generated under white light illumination

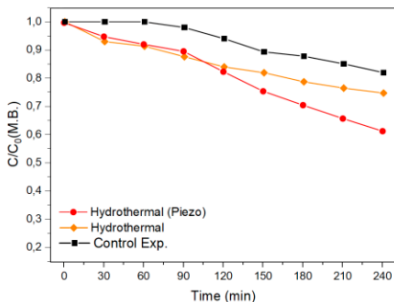


Figure 3. hydrothermal sample Methylene blue photodegradation.

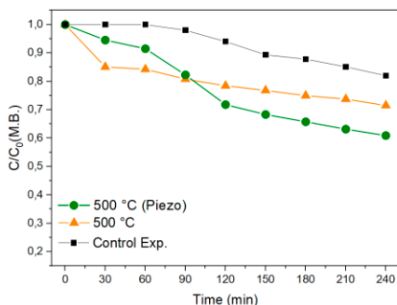


Figure 4. 500 °C sample Methylene blue photodegradation.

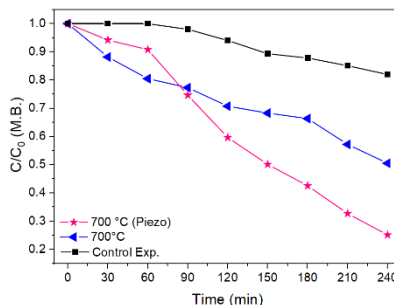


Figure 5. 700 °C sample. Methylene blue photodegradation.

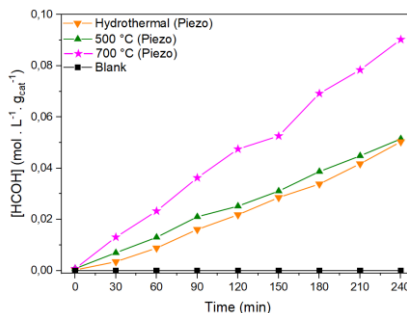


Figure 6. Piezoelectric Methanol Photo-oxidation assays.

Table 1. Methylene Blue and Methanol increases in photodegradation rates under ultrasound effect

Sample	Degradation increase (M.B.)	MeOH oxidation rate (Piezo) ([HCOH] . g ⁻¹ . cat . h ⁻¹)
Hydrothermal	52,1 %	0,01258
500 °C	37,2 %	0,01287
700 °C	51,3 %	0,022565

Conclusions

In this work Bismuth Niobate samples were successfully synthesized through a simple hydrothermal method. The sample treated at 700 °C showed the highest degradation rate for both methylene blue and methanol, presenting an increase of 51,3 % on the photodegradation of the dye under the assistance of the ultrasound. Additionally both the hydrothermal and 500 °C samples showed considerable increases in their photocatalytic activities under the influence of the ultrasound.

Acknowledgments

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