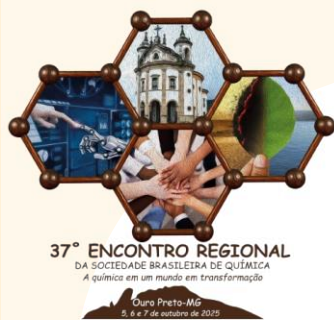




## Hydrothermal Routes for Nb<sub>2</sub>O<sub>5</sub> preparation: Impact of Synthesis Parameters on Photocatalytic Applications

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### ABSTRACT

Niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) nanoparticles were synthesized via microwave-hydrothermal (Nb<sub>2</sub>O<sub>5</sub>-MH) and conventional-hydrothermal (Nb<sub>2</sub>O<sub>5</sub>-CH) methods for photocatalytic hydrogen (H<sub>2</sub>) production. A pseudo-hexagonal crystalline structure was confirmed by XRD patterns and Raman spectroscopy for samples obtained by microwave heating at 140 °C and conventional synthesis at 200 °C. A transition to orthorhombic phase of Nb<sub>2</sub>O<sub>5</sub> was observed for Nb<sub>2</sub>O<sub>5</sub>-CH sample calcinated at 600 °C. FTIR analyses indicated surface hydroxyl groups in as-prepared samples, which contributes for enhanced photocatalytic activity. SEM images revealed spherical particles about 60 nm in sample obtained by microwave conditions. Photocatalytic tests showed that Nb<sub>2</sub>O<sub>5</sub>-MH sample exhibited superior H<sub>2</sub> generation due to surface hydroxyl functionalities promoting charge transfer. This study demonstrates the potential of microwave heating as an efficient, low-cost, and eco-friendly method for producing high-performance niobium pentoxide photocatalysts.

**Keywords:** Nanoparticles, Niobium oxide, Microwave, Photocatalysis, Hydrogen Production.

### Introduction

The supply of safe, clean and sustainable energy is a concern of the 21st century, in order to mitigate the increase of global warming caused by the greenhouse effect of pollutant gases produced by the consumption of fossil and non-renewable fuels. In this context, hydrogen (H<sub>2</sub>) is considered a clean and sustainable alternative of energy source, with potential to substitute fossil fuels in the future. Alternatively, semiconductor-based photocatalysis under light irradiation is a promising, efficient and low-cost process for H<sub>2</sub> generation, and considered an eco-friendly and sustainable technology to produce green energy sources (1). For this technology, the semiconductor materials are a fundamental component to improve its efficiency, therefore, the development of efficient and functional materials to promote the production of alternative fuels is also an urgency. In this context, niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) is a promise candidate material for this application, since it is a stable semiconductor material with a band gap energy value of 3.4 eV which presents a wide range of technological and industrial applications, such as in solar cells, batteries and hydrogen production (2). Additionally, the photocatalytic activity of Nb<sub>2</sub>O<sub>5</sub> is dependent on the oxide structure, which is a direct consequence of the synthesis parameters control and studies on the synthesis methods are relevant to develop efficient ways to obtain Nb<sub>2</sub>O<sub>5</sub> structures with improved photocatalytic activity performance (3). In conventional synthesis methods, high temperatures are necessary to obtain the material in the desired crystalline phase, while via hydrothermal method is possible to control the size, morphology and crystallinity of the particles from low synthesis temperatures. Thus, novel synthesis routes of oxides and control of synthesis parameters have been studied by our research group for improving semiconductor properties. In this work, Nb<sub>2</sub>O<sub>5</sub> nanoparticles were obtained under conventional-hydrothermal and microwave-hydrothermal methods,

### Experimental

#### *Synthesis of Nb<sub>2</sub>O<sub>5</sub>*

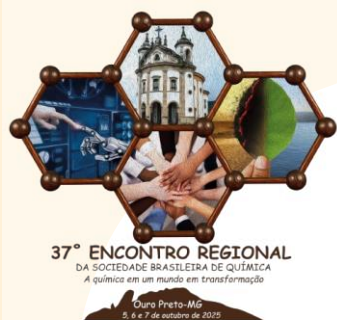
The Nb<sub>2</sub>O<sub>5</sub> sample obtained under microwave-hydrothermal conditions (Nb<sub>2</sub>O<sub>5</sub>-MH) were synthesized by adding 1,5 mmol of niobium ammoniacal oxalate precursor in 40 mL of distilled water and stirred for 15 min for complete precursor dissolution. Then, it was added 1,1 mL of hydrogen peroxide and stirred for 10 min. The formed suspension was transferred and sealed to a Teflon autoclave and submitted to microwave hydrothermal method for 32 min at 140 °C. The final material was washed with water and ethanol and dried at 60 °C for 20 h. A similar procedure was employed to prepare the oxide sample under conventional-hydrothermal conditions (Nb<sub>2</sub>O<sub>5</sub>-CH) for 4 h at 200 °C. The powder obtained was washed with water and ethanol and dried at 60 °C for 20 h. The as-prepared material was calcined in a muffle furnace between 300 °C and 600 °C.

#### *Materials characterization*

The materials were characterized by X-ray diffraction (XRD) on a Shimadzu 6000 (Japan) equipped with CuKα (λ = 1.5406 Å) radiation, Raman spectroscopy on a Horiba LabRAM HR Evolution (Japan) spectrometer with laser excitation of λ = 532 nm, Infrared spectroscopy by Fourier Transform (FTIR) by a PerkinElmer Frontier spectrometer, N<sub>2</sub> physisorption analysis at 77 K in the Micrometrics ASAP 2000 equipment applying BET (Brunauer-Emmett-Teller) model and field-emission scanning electron microscope (FE-SEM, JEOL JSM 6701F).

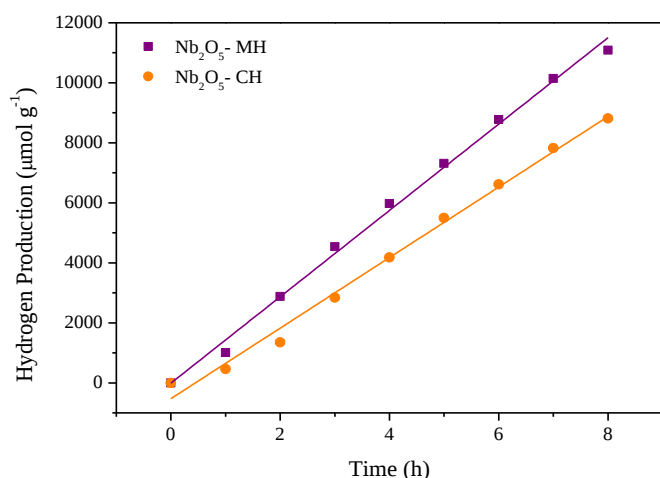
#### *Photocatalytic tests*

The photocatalytic tests of the samples were performed by a deposition of Pt nanoparticles by preparation of a suspension containing 5 mg of the Nb<sub>2</sub>O<sub>5</sub> powders, water, 20% v/v methanol and a H<sub>2</sub>PtCl<sub>6</sub> solution. The suspension was homogenized and exposed to light radiation for 8 h. Aliquots were taken from the reactor and analyzed in a gas chromatograph to monitor H<sub>2</sub> production.



## Results and Discussion

The X-ray diffractograms of the obtained confirmed the formation of pseudohexagonal crystalline structure of  $\text{Nb}_2\text{O}_5$  samples obtained from both methods. However, characteristic peaks of orthorhombic  $\text{Nb}_2\text{O}_5$  structure were exhibited for  $\text{Nb}_2\text{O}_5$ -CH-600 indicating that the crystalline phase of  $\text{Nb}_2\text{O}_5$  is influenced by the calcination temperature. The Raman spectra showed characteristic peaks of pseudohexagonal  $\text{Nb}_2\text{O}_5$  phase for all samples. Large bands attributed to O-H bond stretching were exhibited in the FTIR spectra of the non-calcinated samples of water molecules adsorbed in the surface of the material. A decrease of this band was observed with the increase of calcination temperatures. SEM images showed an aggregate consisting of regular spherical particles with well-defined shapes and medium sizes of approximately 60 nm for  $\text{Nb}_2\text{O}_5$ -MH. The specific surface areas were obtained, and it was verified that the non-calcinated samples exhibited the highest value of specific surface area, around 7 times higher than the  $\text{Nb}_2\text{O}_5$ -CH-600 sample. The photocatalytic results demonstrated that all samples were photoactive, however,  $\text{Nb}_2\text{O}_5$ -MH sample showed a significantly more efficient photoactivity performance in comparison to the as-prepared  $\text{Nb}_2\text{O}_5$ -CH sample and to the calcinated ones, indicating that microwave hydrothermal method played an important role in the preparation and in the photoactivity of niobium pentoxide and has advantages in terms of energy savings. Also, the presence of the hydroxyl functional groups absorbed on the surface of oxide improves photocatalytic activity of the samples. Figure 1 shows the photoactivity of both microwave and conventional conditions synthesized  $\text{Nb}_2\text{O}_5$  to promote hydrogen generation. Additionally, studies of the optimization of synthesis and photocatalytic properties of niobium oxide, as well as its efficiency to promote hydrogen reduction reaction by water splitting experiments are being carried out.



**Figure 1.** Photocatalytic hydrogen evolution for  $\text{Nb}_2\text{O}_5$  catalysts.

## Conclusions

Crystalline niobium pentoxide nanoparticles were successfully obtained under different synthesis conditions, which played an important role in the structural, surface properties and in the application of the synthesized samples as photocatalysts. Crystalline  $\text{Nb}_2\text{O}_5$  pseudohexagonal structure was obtained via microwave at lower temperature and significantly shorter reaction time when spectroscopy compared to the  $\text{Nb}_2\text{O}_5$  sample obtained by conventional-hydrothermal method.  $\text{Nb}_2\text{O}_5$  prepared via microwave showed higher photoactivity and the increase of calcination temperature reduced the photocatalytic activity of the samples due to the removal of functional groups adsorbed in the surface of the materials. This work proposes a high performance  $\text{Nb}_2\text{O}_5$  photocatalyst obtained by a facile, low-cost and ecological synthesis method.

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