



## The influence of the hydrothermal treatment pH on the photoactivity of Nb<sub>2</sub>O<sub>5</sub>

Paulo H. H. Nunes<sup>1</sup>, Adrielle D. Santos<sup>1</sup>, Higor de O. Alves<sup>1</sup>, Lucas L. Nascimento<sup>1</sup>, Rafael

A. C. Souza<sup>3</sup> and Antonio O. T. Patrocínio<sup>1,2\*</sup>

<sup>1</sup>*Laboratório de Fotoquímica e Ciência dos Materiais, LAFOT-CM Instituto de Química, Universidade Federal de Uberlândia, 38400-902, Uberlândia, MG, Brasil.*

<sup>2</sup>*Centro de Excelência em Hidrogênio e Tecnologias Energéticas Sustentáveis – CETHS, Parque Tecnológico Samambaia, 74690-631, Goiânia, GO, Brazil.*

<sup>3</sup>*Faculdade De Ciências Exatas E Tecnologia–FACET, Departamento de Ciências Exatas, Universidade Federal de Grande Dourados, 79084-970, Dourados, MS, Brasil*

*\*Corresponding author. E-mail: otaviopatrocinio@ufu.br*

### ABSTRACT

Photocatalysis has drawn the attention of researchers worldwide as a promising sustainable approach to reduce fossil fuel dependency, thus decreasing the advance of the greenhouse effect. In this context, Nb<sub>2</sub>O<sub>5</sub> is a wide bandgap semiconductor, with good synthetic versatility, as its structural and morphological parameters can be tuned with ease. In the present work, pristine Nb<sub>2</sub>O<sub>5</sub> was modified by changing the pH of the hydrothermal media. The properties of the resulting materials were rationalized based on the synthesis pH, and they were tested against H<sub>2</sub> evolution assays, using methanol as a sacrificing agent. Only the material obtained at pH = 8 was able to produce H<sub>2</sub>, which was attributed to the higher incidence of structural defects induced by hydroxyl ions, allowing improved charged transfer between the photocatalyst and the Pt co-catalyst.

**Keywords:** Green Hydrogen; Hydrothermal treatment; Nb<sub>2</sub>O<sub>5</sub>; Niobium; Photocatalysis.

### INTRODUCTION

Recent efforts to reduce global energy dependency upon fossil fuels have driven research on alternative and clean energy sources. In this scenario, solar energy is highlighted, as it has the potential to supply the whole global energy demand [1]. However, there are still challenges to be overcome to enable practical solutions for efficiently harvesting sunlight.



Among the many techniques that can be employed to convert solar energy, photocatalysis stands out as the less complex and most cost-effective alternative [2]. Usually, this process is accomplished by semiconductor oxides, which must have suitable bandgap energy and band edge positions, high surface area and chemical stability [3]. Niobium oxide is a promising photocatalyst with similar properties when compared to  $\text{TiO}_2$ , but with a more negative conduction band energy and lower recombination kinetics, at the cost of higher band gap energy ( $\sim 3.3$  eV) and, thus, lower visible light absorption [4]. Therefore, despite its limitations,  $\text{Nb}_2\text{O}_5$  can be efficiently applied for promoting light induced reactions, such as hydrogen evolution.

In this work, a series of photocatalysts were obtained through the hydrothermal treatment of  $\text{Nb}_2\text{O}_5$  at different pHs, aiming at investigating the influence of the hydrothermal pH media in the performance of the materials against photocatalytic hydrogen evolution.

## MATERIALS AND METHODS

The studied photocatalysts were obtained through hydrothermal treatment, in which 0.500 g of pristine  $\text{Nb}_2\text{O}_5$  were suspended in 80 ml of deionized water under constant magnetic stirring. Subsequently, the suspension's pH was adjusted to 2, 4, 6, 8 and 10 with 0.1 M solutions of  $\text{NH}_4\text{OH}$  or  $\text{HNO}_3$ . Afterwards, the resulting suspension underwent 24 hours of hydrothermal treatment at 200 °C. Lastly, all samples were centrifuged, washed and dried at 80 °C.

The photocatalytic  $\text{H}_2$  evolution assays were carried out in septum-sealed 80 or 18 mL borosilicate jacketed reactors. Both were connected to a thermostatic bath set at 20 °C. In all assays, 1 mg  $\text{mL}^{-1}$  of photocatalyst were suspended in 10% v/v of MeOH aqueous solution and kept under constant magnetic stirring. A 300 W xenon was used as an irradiation source. The irradiance was set at 100  $\text{mW cm}^{-2}$ . To improve the photocatalytic  $\text{H}_2$  evolution, 1%  $\text{Pt}^0$  content was deposited onto the photocatalysts surface through the *in situ* Photodeposition method, as described elsewhere [5].

## RESULTS AND DISCUSSION

The XRD patterns of Nb<sub>2</sub>O<sub>5</sub> prior and after the hydrothermal treatment are shown in Fig 1a. The pristine Nb<sub>2</sub>O<sub>5</sub> and those treated at pH 2, 4 and 6 presented a mixture of orthorhombic (T-Nb<sub>2</sub>O<sub>5</sub>) and monoclinic (H-Nb<sub>2</sub>O<sub>5</sub>) phases, according to powder diffraction files ICDD 30-0873 and 37-1468, respectively. For the sample treated at pH 8 only the pseudo-hexagonal (TT-Nb<sub>2</sub>O<sub>5</sub>) structure was observed (ICDD 28-0317), indicating a phase transition. The long-range structural organization of the samples prepared at alkaline medium was severely reduced, especially at pH = 10, in which only two broad features can be seen in its diffractogram.

It is known that TT-Nb<sub>2</sub>O<sub>5</sub> phase may be stabilized by defects in the structure, for example the replacement of oxygen atoms by vacancies or by monovalent species, such as OH<sup>-</sup> and Cl<sup>-</sup> impurities [6]. Therefore, the hydrothermal treatment promotes the formation of TT-Nb<sub>2</sub>O<sub>5</sub> phase in alkaline medium, where the hydroxyls guarantee its stability. Furthermore, according to XRD, as the concentration of OH<sup>-</sup> ions increase, the number of defects in the material's structure and, consequently, its crystallinity decreases until reaching a point where the structural defects are so many that the material becomes amorphous, as observed in the pH 10 sample.

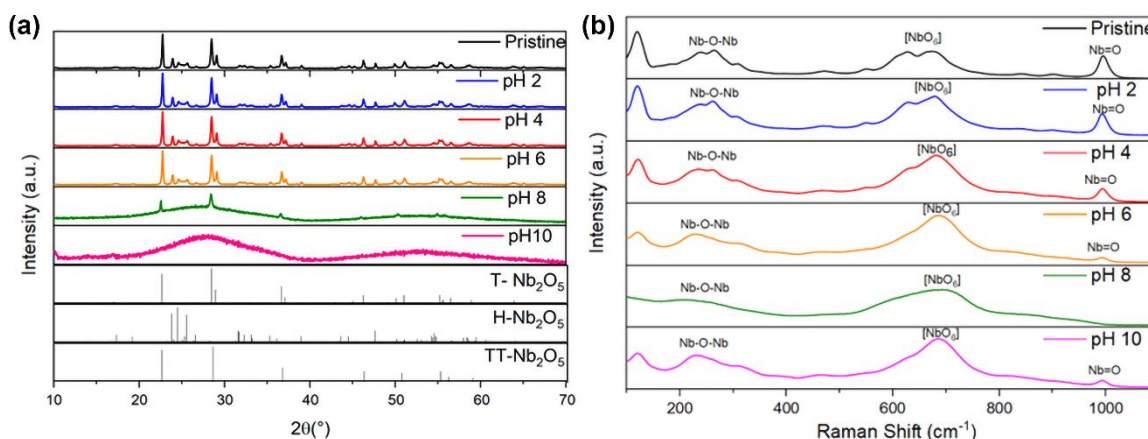


Figure 1. (a) XRD patterns and (b) Raman spectra of the Nb<sub>2</sub>O<sub>5</sub> samples.

Raman spectroscopy analyses, Fig 1b, agrees well with the XRD data, confirming the presence of H-Nb<sub>2</sub>O<sub>5</sub>, T-Nb<sub>2</sub>O<sub>5</sub> and TT-Nb<sub>2</sub>O<sub>5</sub> phases. Vibrational modes below 200 cm<sup>-1</sup> refer to Lattice vibrations, and these bands are present in the H-Nb<sub>2</sub>O<sub>5</sub> and T-Nb<sub>2</sub>O<sub>5</sub> phases. The bands observed near 200-300 cm<sup>-1</sup> can be attributed to the bending modes of the Nb-O-Nb linkages, while the prominent band



in the region of 550-800  $\text{cm}^{-1}$  corresponds to the symmetric stretching modes of the  $[\text{NbO}_6]$  polyhedral [7]. Although the amorphous sample treated at pH 10 does not present long range order, it does have short range order, as its Raman spectrum also shows a variety of bands, resulting from a non-stoichiometric mixture of slightly distorted polyhedra of  $\text{NbO}_6$ ,  $\text{NbO}_7$  and  $\text{NbO}_8$  [7].

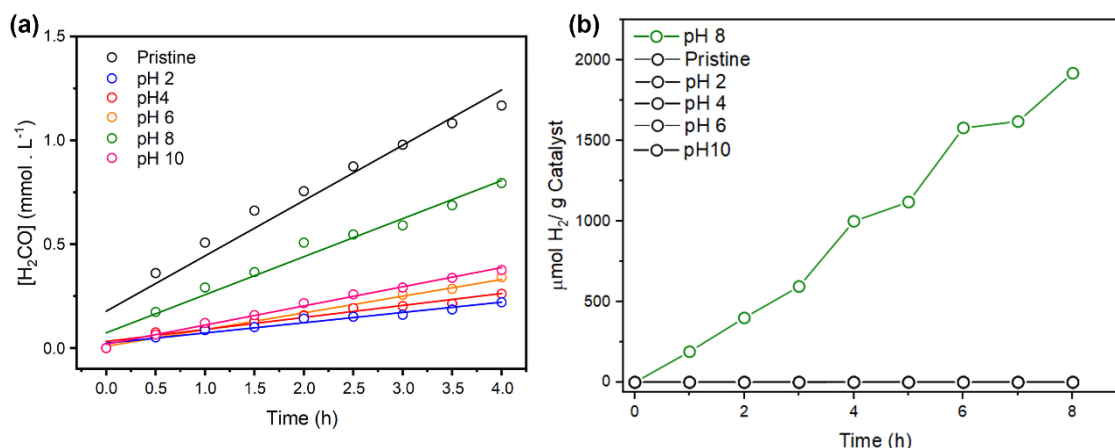


Figure 2. (a) Methanal production and (b) hydrogen evolution during the photocatalytic experiments using Pt loaded  $\text{Nb}_2\text{O}_5$  samples.

Different photocatalytic activities for each of the phases found in this work are reported in literature, whereas the H phase is reported as the most photoactive, mainly due to the oxygen vacancies present in this structure [6, 8]. This would explain the fact that pristine  $\text{Nb}_2\text{O}_5$  presents the best photocatalytic activity during methanol photodegradation tests, Fig 3a, achieving much higher methanal production.

The sample  $\text{Nb}_2\text{O}_5$  pH 8 loaded with  $\text{Pt}^0$  (1% wt.) was the only one able to produce  $\text{H}_2$ , Fig 3b. The electronic transition between the d orbitals of  $\text{Nb}^{5+}$  and  $\text{Pt}^+$  is forbidden for the H-  $\text{Nb}_2\text{O}_5$  phase contained in pristine  $\text{Nb}_2\text{O}_5$  and the samples treated at acid pH, while in the T- $\text{Nb}_2\text{O}_5$  phase this transition is partially allowed [8]. This can be explained through Laporte's Rule, where electronic transitions that conserve parity are prohibited. Due to the symmetrical octahedron of  $\text{NbO}_6$  present in these two phases, the electronic transition is hampered, preventing the evolution of  $\text{H}_2$ . Similarly, the TT- $\text{Nb}_2\text{O}_5$  phase presents significant structural distortions due



to the insertion of OH<sup>-</sup> ions, which makes the transition allowed, making the photocatalytic evolution of H<sub>2</sub> possible.

## CONCLUSION

A series of photocatalysts were obtained by controlling the pH of the hydrothermal treatment media. The samples obtained in acid media retained the structural properties of pristine Nb<sub>2</sub>O<sub>5</sub> while the samples synthesized in alkaline media showed a lower degree of crystallinity with significant presence of structural defects. Although the pristine Nb<sub>2</sub>O<sub>5</sub> achieved higher methanol photodegradation yields, the material obtained at pH 8 was the only sample capable of producing H<sub>2</sub> using methanol as sacrifice agent. The improved H<sub>2</sub> production was attributed to the presence of structural defects induced by hydroxyl ions, which allowed improved charged transfer between the photocatalyst and the Pt co-catalyst.

Therefore, the present work brings a cost-effective approach for tuning materials for photo-induced green H<sub>2</sub> production

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