

Optical and Structural Characterization of $\text{Bi}_2\text{Fe}_x\text{NbO}_7$ Nanoparticles for Environmental Applications

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Abstract

Photocatalytic materials development is very important from an environmental perspective. They can be employed in clean energy production by hydrogen generation as well as in wastewater treatment by photocatalysis. One of the key subjects in this area is the advancement of materials with a low band gap, thus the catalyst can use the sunlight more efficiently. Based on this issue, this research aims to develop photocatalysts based on bismuth, niobium, and iron ($\text{Bi}_2\text{Fe}_x\text{NbO}_7$), analyze the influence of iron concentration ($x = 0, 0.8, 1, \text{ and } 1.2$) and characterize them through optical and structural analysis. The powder samples were synthesized by the sol-gel method. Band gap estimation was performed using UV-Vis analysis and the Kubelka-Munk method. The XRD technique was employed for phase determination and structural characterization. The catalyst with no iron (Bi_2NbO_7) presented a mix of three phases of reagents and a band gap of 3.14 eV. The iron addition promotes crystalline photocatalysts with high visible light absorption ability and a lower band gap, 2.09 eV. Further analysis must be performed. However, based on structural and optical proprieties, these materials can efficiently be employed both in wastewater treatment and hydrogen production.

Keywords:

Photocatalysts;
Hydrogen Production;
Bismuth;
 $\text{Bi}_2\text{Fe}_x\text{NbO}_7$;
Band Gap.

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1- Introduction

Recently, the scientific community has shown a crescent interest in photocatalytic materials for environmental applications, since the use of these materials might lead to the development of sustainable technologies that allow cleaning the environment in a safe and effective way. Besides, they can be employed in clean energy production by the hydrogen economy [1].

Photocatalysts are semiconductor materials that contain an electronic band gap (E_g), which represents the energy edge between the conduction and valence band. When these materials are irradiated by a photon with similar or higher energy than the band gap, an electron is promoted to the conduction band and an electron hole is generated in the valence band. These electronic beings are known as electron-hole pairs [2]. There are two main environmental applications for the electron-hole pair: water splitting and photocatalysis.

The water splitting technique (Figure 1a) began with Fujishima and Honda (1972) [3]. They present an irradiated TiO_2 semiconductor photo-anode. The electron-hole pair generated first oxidized the water into H^+ ions and O_2 gas at the TiO_2 photo-anode. Then, the H^+ ions were reduced to H_2 gas in a platinum cathode. H_2 production is an important and clean energy carrier, which can lead to an environmentally friendly energy matrix and eliminate the need for fossil fuels.

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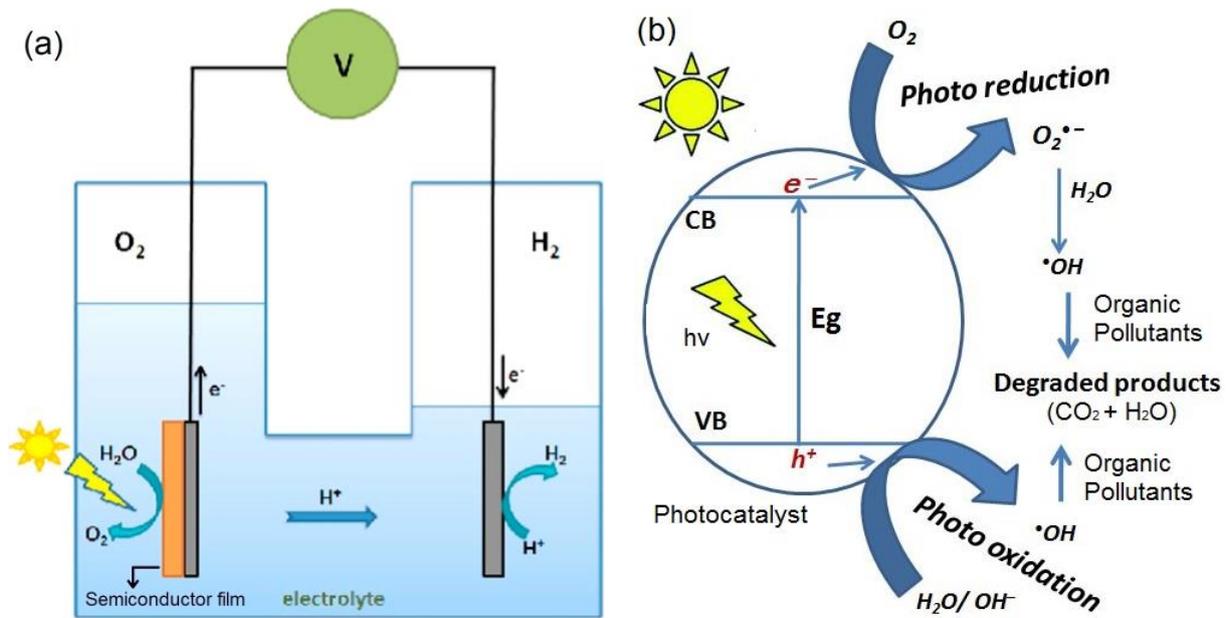


Figure 1. (a) Honda and Fujishima water splitting scheme for hydrogen evolution [4]; and (b) Photocatalysis wastewater treatment process. Adapted from Kumar et al., (2017) [5].

Another important application is the wastewater treatment process known as photocatalysis (Figure 1b), an Advanced Oxidative Process (AOP). When the electron-hole is generated, it produces free radicals with a very high oxidative potential. Thus, it is recognized as a very efficient technique, since these radicals can mineralize the organic pollutants to CO_2 and H_2O , eliminating all the pollutants [6].

For these both mentioned processes, there are, among others, a key required propriety: low band gap energy. As the electron-hole pair is generated when the incident photon presents energy equal or higher than the band gap, and as the electron-hole pair is what is required to start the photocatalytic processes, semiconductors with low band gap can be more efficient. In addition, the smaller the band gap of the material, the greater the quantity of photons with the energy required to activate it [7].

Recently, photocatalysts based on bismuth, such as bismuth mixed oxide semiconductors have attracted interest, mainly due to their excellent stability, visible light absorption and photocatalytic properties. Included among others are bismuth oxide (Bi_2O_3), bismuth niobate (Bi_3NbO_7), bismuth ferrite ($\text{Bi}_2\text{Fe}_4\text{O}_9$) and perovskite bismuth ferrite (BiFeO) [8].

In their research, Roper-Vega et al., (2010) [9] reports the sol-gel synthesis of Bi-M-Nb-O thin films, where in M position were tested aluminum, gallium, indium and iron. The gallium-containing film presented the highest crystallinity among the films. Iron-containing film ($\text{Bi}_2\text{FeNbO}_7$) exhibited the lowest band gap value (2.47 eV), and higher efficiency in hydrogen generation and phenol degradation due to the introduction of iron atoms, which also formed the Bi_2O_3 and BiFeO_3 phases. Bencina et al., (2014) have shown that Bi-Fe-Nb-O nanoparticles exhibit intense visible-light absorption, narrow band gap and a higher photocatalytic activity than $\text{Bi}_2\text{Ti}_2\text{O}_7$ nanoparticles of the similar size and commercial TiO_2 -P25. The Bi-Fe-Nb-O powder was also stable and reusable.

Based on these questions, this research work targets to develop photocatalysts based on bismuth, niobium and iron. It aims to evaluate the effect of iron addition on the Bi-Fe-Nb-O system through optical and structural analysis. Nonetheless, seeks to evaluate the results and possible environmental applicability.

2- Research Methodology

In order to develop and characterize photocatalysts based on bismuth, niobium and iron ($\text{Bi}_2\text{FeNbO}_7$) for environmental applications, powders were synthesized by sol-gel method. Four compositions were proposed, one without iron (Bi_2NbO_7) and with 0.8, 1.0 and 1.2 mole of iron ($\text{Bi}_2\text{Fe}_{0.8}\text{NbO}_7$; $\text{Bi}_2\text{FeNbO}_7$ e $\text{Bi}_2\text{Fe}_{1.2}\text{NbO}_7$), aiming to evaluate the iron influence on the photocatalytic proprieties of this semiconductor materials. Figure 2 shows the methodology flowchart applied to this research.

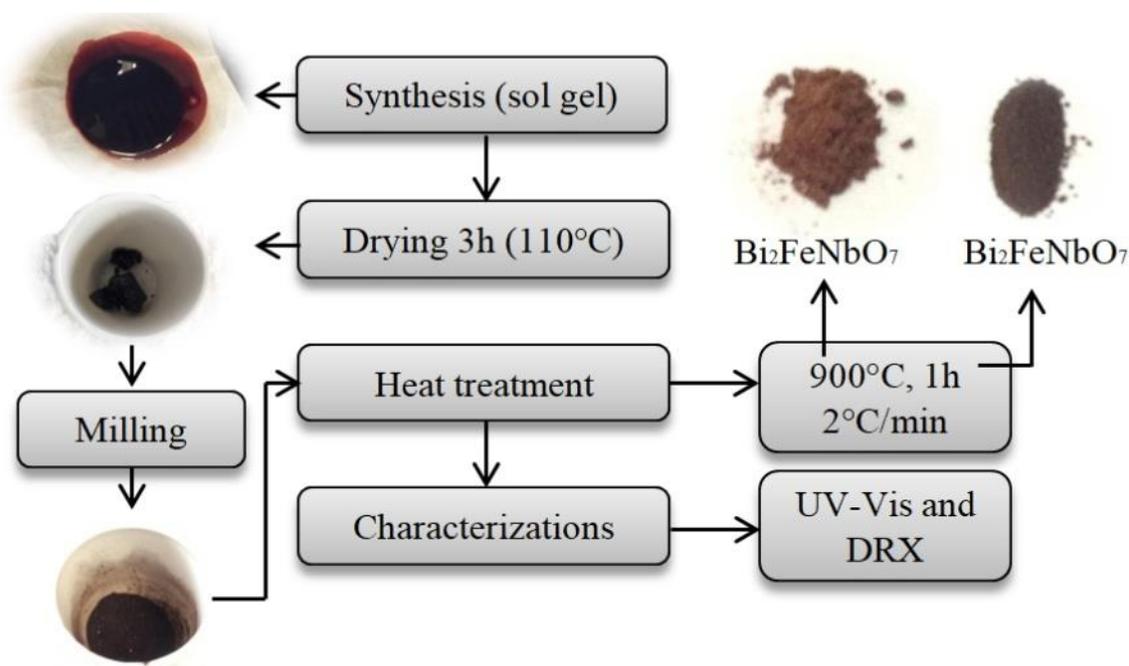


Figure 2. Research methodology flowchart.

The catalysts were prepared in three stages: firstly, stoichiometric amounts of metal precursor ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{Synth}$) were diluted in 5 ml of Acetylacetonone (Sigma-Aldrich) under magnetic stirring for 15 minutes. Parallel to this process, stoichiometric quantities of ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/\text{Vetec}$) were solubilized in 5 ml of Acetylacetonone under magnetic stirring for 15 minutes. Niobium chloride (NbCl_5) was solubilized in 4 ml of hydrochloric acid under magnetic stirring for 5 minutes. Secondly, after total solubilisation of both, the solution containing bismuth was homogenized with the solution containing iron. Then, finally, the niobium containing solution was titrated to the above, kept under constant stirring until complete homogenization, forming a uniform orange-yellow coloration sol. More details of this synthesis were published elsewhere [10].

Subsequently, the four samples of sol were dried in an oven at 110°C for 1h to evaporate the solvents and then heat-treated at 900°C . A slow heating rate (2°C min^{-1}) and 1h maximum temperature was used aiming to produce powders with good crystallinity.

In the area of catalytic materials for environmental proposes, it is essential to obtain information about the band gap value of the material. The Kubelka-Munk method was utilized in the diffuse reflectance mode for band gap estimation. A Cary 5000 UV-Vis spectrometer was used to measurement. The Kubelka-Munk function is described by Myrick et al., (2011) [11] (Equation 1), where k is the absorption coefficient and s is the scattering factor.

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s} \quad (1)$$

The direct band gap energy (E_g , eV) was obtained by plotting $F(R) \cdot h\nu^2$ vs E_g ($1240/\lambda_g$) extrapolation of the rising part of the curve to the x-axis (λ_g , nm).

The crystallinity of the obtained catalysts was evaluated using the X-Ray Diffraction (XRD) technique. The crystalline phases were identified using a 2θ angle between 10° and 70° through the Joint Committee on Powder Diffraction Standards (JCPDS) database and with the aid of the *X'Pert High Score* software. It was used a Philips diffractometer, X'Pert MDP model, Cu $K\alpha$ radiation tube ($\lambda=1.5418 \text{ \AA}$), operating at 40 kV and 40 mA.

3- Results and Discussion

The XRD patterns of all samples are shown in Figure 3. As can be inferred in Figure 3a, the catalyst without iron (Bi_2NbO_7) presented a mix of three phases: Bi_3NbO_7 , identified by the crystallographic card JSCP 01-086-0875; Nb_2O_5 , JSCP 01-074-0298 and Bi_2O_3 crystallographic card JSCP 01-074-1373. All these materials are reported in the literature as stable photocatalysts. Zhang et al., (2014) [12] synthesized $\text{Bi}_2\text{O}_3/\text{g-C}_3\text{N}_4$ and investigated its activity in photocatalysis. They found a high efficiency in the UV spectra and a band gap of 3.34 eV. Bi_3NbO_7 nanosheets were synthesized by Wang et al., (2016) [13]. They have achieved a high Rhodamine B degradation under visible radiation and band gap around 2.6 eV. Nb_2O_5 was added to TiO_2 to produce photo anodes. The performance in solar energy conversion was increased in 20% [14].

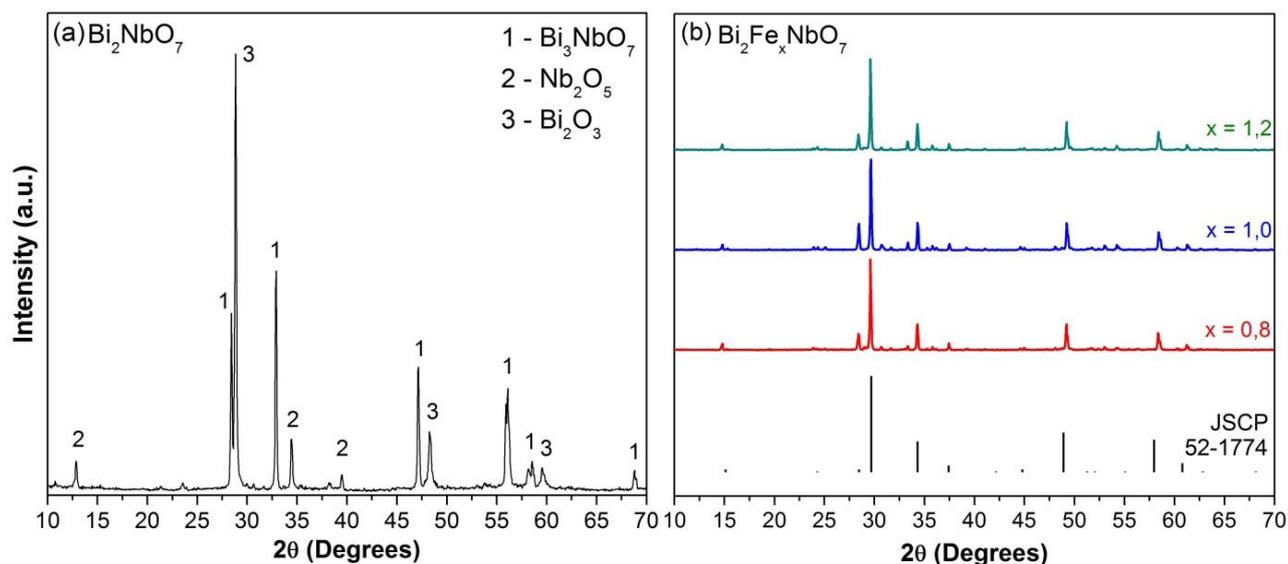


Figure 3. XRD patterns of the catalysts annealed in 900°C, (a) Bi_2NbO_7 and (b) $\text{Bi}_2\text{Fe}_x\text{NbO}_7$.

Figure 3b shows the patterns for the Fe-containing samples. All the main pics are referred to the crystallographic card JSCP 52-1774, as can be seen in the graph. The iron addition apparently does not change the crystallographic structure of the materials in the analyzed level. It is important to note that the nomenclature $\text{Bi}_2\text{Fe}_x\text{NbO}_7$ is given due to the stoichiometric quantities employed in the synthesis of catalysts. The unique JSCP card record representing this oxide in the PDF2 database of the X'Pert High Score software (52-1774) exhibits the formula $\text{Bi}_{1.34}\text{Fe}_{0.66}\text{Nb}_{1.34}\text{O}_{6.35}$, indexed by Radha et al., (2018) [15]. The same authors performed Rietveld refinement of this oxide, identifying cubic pyrochlore structure, Fd-3m space group and unit cell volume of $1155,645 \text{ \AA}^3$.

To determinate the absorption ability of materials, we measured their absorption spectra with diffuse reflectance analysis (Figure 3). The sample without iron (Bi_2NbO_7) showed maximum wavelength absorption at 430 nm approximately. The iron containing showed that maximum absorption spectra shifted towards longer wavelengths, about 620 nm, in visible spectrum.

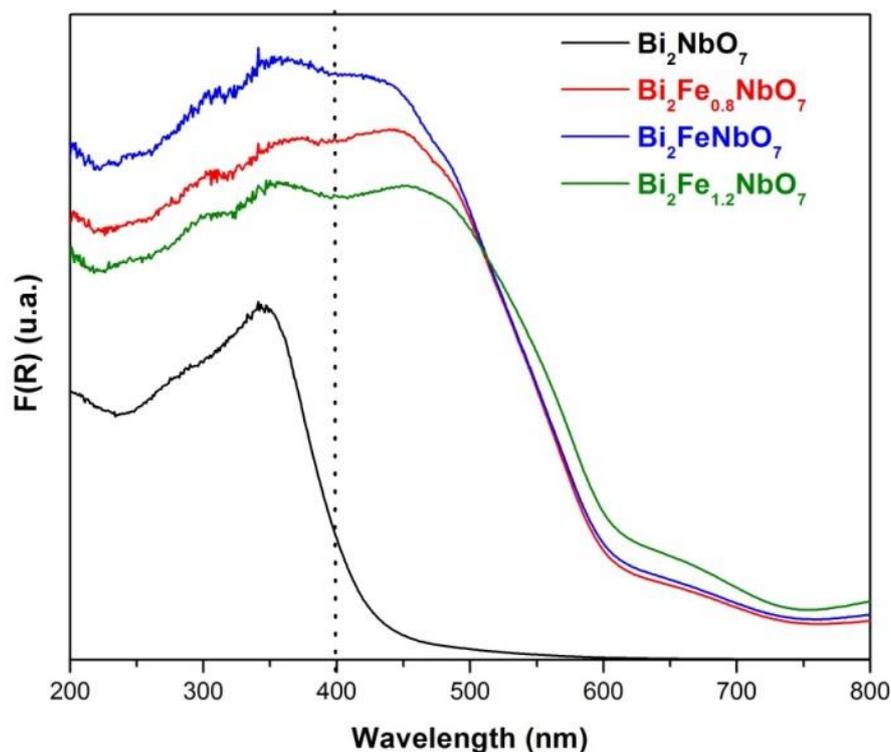


Figure 4. Diffuse reflectance UV-Vis spectra of $\text{Bi}_2\text{Fe}_x\text{NbO}_7$ catalysts plotted as Kubelka-Munk function $F(R)$ of the reflectance, R .

The band gap was estimated from UV-Vis diffuse reflectance of the powders by Kubelka-Munk function as described previously. The catalyst with no iron presented a direct band gap of 3.14 eV. It was possible to observe that the addition of iron provides a decrease in this value, and the sample with the most concentration ($\text{Bi}_2\text{Fe}_{1.2}\text{NbO}_7$) has the smallest band gap (2.09 eV). Thus, as the band gap is a fundamental propriety for environmental applications, the iron addition probably provides a semiconductor more efficient in operation than the material without it.

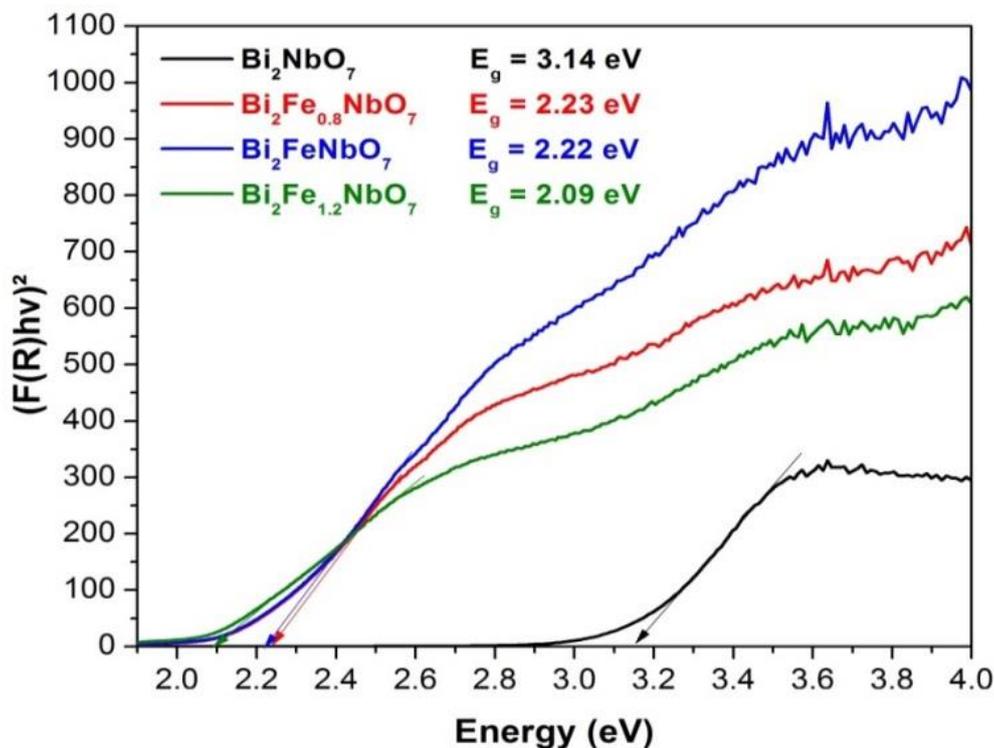


Figure 5. Band gap estimation of $\text{Bi}_2\text{Fe}_x\text{NbO}_7$ photocatalysts.

There are several possible explanations for this phenomenon. One of the most recurrent and established claims that the insertion of iron, which is a conductive metal, produces intermediate energy levels between the valence band and conduction band, compared to samples without it [16]. Then the material is able to absorb a larger part of the solar spectrum as it requires less energy photons to promote the electrons from their valence band to the conduction band. This phenomenon is known as redshift [17], and is accompanied by a change in yellowish white color from ironless powders (Bi_2NbO_7) to light brown at the highest concentration ($\text{Bi}_2\text{Fe}_{1.2}\text{NbO}_7$).

The decrease in the band gap value may also be related to the higher crystallinity presented by iron containing catalysts. As illustrated by the X-ray diffractogram (Figure 2), the powders with iron show higher crystallinity and therefore fewer amorphous parts than Bi_2NbO_7 , which is composed by three phases. Crystalline materials exhibit greater organization and long-range repetition of the overall structure. Thus, the conduction and valence bands of these materials are more uniform, which may contribute to the reduction of the band gap value measured in Fe-containing photocatalysts.

As a major result, we found in this research that iron increasing promotes a catalyst with lower band gap, able to absorb longer wavelengths. Table 1 illustrates a comparison between the band gap energy of the catalyst produced in the best configuration ($\text{Bi}_2\text{Fe}_{1.2}\text{NbO}_7$, 2.09eV) with some other bismuth-based catalysts in the literature.

Table 1. Comparison between band gap from this research and literature.

Catalyst	Sample	Band gap (eV)	Ref.
BiVO_4	Films (210 nm)	2.35	[18]
$\text{Bi}_{0.84}\text{La}_{0.16}\text{FeO}_3$	Powder (15 nm)	2.05	[19]
$\text{Bi}_{0.84}\text{Gd}_{0.16}\text{FeO}_3$	Powder (17 nm)	1.92	
Bi-Fe-Nb-O	Powder (40 nm)	2.60	[7]
$\text{Bi}_2\text{GaNbO}_7$	Films (4 μm)	2.67	[9]

4- Conclusion

It was possible to produce promising photocatalysts by the sol-gel method. The catalyst with no iron (Bi_2NbO_7) presented a mix of three phases, from the reagents. Regarding optical properties, it has shown a lower light absorption capacity and, hence, a bigger band gap energy of 3.14 eV. It was possible to infer that iron addition promotes higher absorption and thus a band gap of 2.09 eV, as well as more pure and crystalline photocatalysts. These are very good properties if compared with other bismuth-based photocatalysts. Further analysis must be performed. However, based on structural and optical properties, these materials can efficiently be employed both in wastewater treatment by photocatalysis and hydrogen production by photo electrolysis. The main advantages are the crystallinity and low band gap conferred on the material; thus, it can absorb the visible spectrum of solar radiation.

5- Funding and Acknowledgments

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6- Conflict of Interest

The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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